Multiple Cryogenic Packed Bed Dehydration and Separation of CO_2 and Hydrocarbons from Natural Gas

by

Muhammad Ali Redza bin Ab Halim

Dissertation submitted in partial fulfillment of
the requirements for the
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CERTIFICATION OF APPROVAL

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Approved by,

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(Prof. Dr. Saibal Ganguly)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
SEPTEMBER 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MUHAMMAD ALI REDZA BIN AB HALIM
13201

ABSTRACT

A state-of-the-art methods for CO_2 and water separation from natural gas is presented using multiple cryogenic packed beds. The main concept for such separation is the difference in freezing points on each component in natural gas stream. A series of pre-cooled beds for separation of water, CO_2 and natural gas are used in this study. Both dehydration and CO_2 removal process are kept slightly below the freezing point of water and CO_2, respectively. It will undergo desublimation process, where vapor directly change phase to solid. The remaining components are unaffected and stay in vapor form. The dehydration process using cryogenic packed bed are studied in the temperature ranging from 0°C to -30°C. While the experiment for CO_2 removal are studied at -70°C to -100°C. The statistical optimization of natural gas separation are studied through simulation at high pressure and atmospheric pressure using cryogenic packed bed.

ACKNOWLEDGEMENT

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background Study

Natural gas plays an important role in generating electricity and home appliances usage. Malaysia is said to be in the top 5 in Asia Pacific of gas reserve holder, estimated almost 85 trillion cubic feet (Roussak, 2013). Most of the reserves are located at eastern area, predominantly offshore Sarawak. The capability of producing natural gas has been one of the focus area for researchers in finding the best way to extract natural gas from well and purify it before reaching the end user.

Table 1: High CO_2 Content Field in Malaysia

Holder	Field	CO_2 content (%)	Total (TSCF)
PCSB	Beranang	28	0.08
PCSB	Bergading	40	1.36
PETRONAS	Bujang	66	1.47
PETRONAS	J5	87	5.37

The average composition of CO_2 in Malaysian natural gas well ranges around 30 mole% and some of the fields may reach 80 mole% (Nasir, 2006). Some companies in the industry use membrane method to remove the high CO_2 content due to their high recovery expectations of products. In addition, membrane are simple, versatile and have low capital investment and operation. But, there are several drawbacks when using membrane for CO_2 separation such as recompression of permeate, having moderate purity and operating problem of membrane under high pressure (Shimekit & Mukhtar, 2012).

Some companies are still using solvent to capture CO_2 from natural gas stream. Amines are very common solvent to be used in this purpose. They consume low energy and require low operating and maintenance cost. But, to invest in this technology, the companies have to wait longer for delivery time and on-site installation. The use solvent size of equipment become prohibitive for high percentage of CO_2 in feed.

Apart from the mentioned technologies to capture CO_2 from natural gas such as adsorption, pressure swing adsorption and membrane method, cryogenic separation provide a sound alternative in the industry. Cooling feed gas at very low temperatures enhances change of phase of certain components; thus capturing particular components with phase change. In present study, CO_2 will be removed from natural gas stream to obtain higher purity of hydrocarbon. As CO_2 solidified at different temperature compared to the crucial hydrocarbon such as methane, the main subject of the present study is the characterization of engineering parameters for separation.

Individually, CO_2 freeze at -78°C while methane solidifies at much more lower temperature of -182°C at standard temperature and pressure (STP). The huge difference in freezing point of both components make this capturing technique a realistic one. It is fully utilized to determine the best operating condition for the natural gas sweetening.

1.2 Problem Statement

CO_2 separation has always been the main concern in purifying natural gas stream. It is indeed the major process in any offshore plant in Malaysia. The high-CO_2-content natural gas force researchers to come out with new technology to fully capture the acidic gas. Recent studies had shown that cryogenic method can be used on the offshore platform to cater to this problem. It is in conceptual stage and has not been tested in an industrial-scale in this region. Theoretically, due to the difference in freezing points of components in natural gas from high pressure natural gas flow in pipeline, they can be separated in multi stage cryogenic cooler network using cryogenic temperatures. Only lighter hydrocarbons such as methane and ethane remain in gaseous state due to their very low freezing points.

1.3 Objective

The main objectives of this study are:

i. To study the optimal separation of CO_2 from natural gas using cryogenic multi-bed networks

ii. To simulate the effectiveness of low-temperature CO_2 capture from hydrocarbon mixtures in natural gas

iii. To propose a feasible model of cryogenic capture method

iv. To study the best operating conditions for dehydration unit and CO_2 removal unit experimentally

1.4 Scope of the Study

In this study, the main subjects under investigation are:

i. Composition and thermodynamics of Malaysian Natural Gas

ii. Statistical optimization of Cryogenic conditions for high-pressure flow line from natural gas pipeline

iii. Experimental studies using cryogenic packed bed

1.5 The Relevancy of the Project

The separation of CO_2 from natural gas using cryogenic methods is an applicable methods to be further studied. The concept of differences in freezing points is fully utilized in developing CO_2 capture technique. Different components condense and desublimate at different rate and condition. This method is suitable for high CO_2 concentration natural gas stream as it focuses on the CO_2 rather than other components. Hence, providing thoughtful insight on the improvement of the method clarifies the pros and cons of the proposed methods.

1.6 The Feasibility of the Study

The study is commenced by collecting data regarding the scope of the project through journals, books and technical papers, specifically on the cryogenic methods of separating CO_2 from gas feed and the thermodynamics data of CO_2 in multi-component mixture. The study is conducted in stage by stage manner to capture the main concept and the area that need to be focused on. Statistical optimization study is used to determine the optimum condition to be further observed experimentally. Next, laboratory experiment is conducted on CO_2 removal and dehydration. Critical analysis of data and experimental results are emphasized to ensure the accuracy and the relevancy of the proposed project.

The time frame and the equipment in the laboratory are prepared for the execution of the project. The project should be successfully carried out with the help of post graduate students and laboratory technician that have thorough experience in handling the apparatus and knowledge in the field.

CHAPTER 2

LITERATURE REVIEW

2.1 Cryogenic Processing Methods

Cryogenic separation or also known as low- temperature separation uses a very low temperature levels below 120 K or -153°C (Leuven, 2007) . In extraction of lighter hydrocarbons such as ethane, cryogenic method is favored over other methods. Some applications use turbo expander to lower down the temperature of gas feed, and some others uses external refrigerants. The sudden cool from turbo expander capable of desublime the CO_2 but keep lighter components at gaseous state (Ewan, 1975) . But there are some drawbacks of cryogenic separation. It need high energy intensive for regeneration and can lower down the overall plant efficiency when applied to streams with low CO_2 concentration. In addition, the percentage for blockage of process equipment by dry ice or hydrate is high.

Some of the literature (Berstad, et. al, 2012) uses -90°C, hence the natural gas conditioning is not considered as 'cryogenic', but rather low-temperature. The rigid specification for the model is CO_2 concentration in the natural gas stream for liquefaction is to be maximum 50 ppm. Berstad et. al estimated product streams, power consumption for auxiliary refrigeration and steam requirement using low- temperature CO_2 capture technology. They came out with combination of distillation and extractive distillation using three low- temperature column that reduce the concentration of CO_2 from 50.6% to 50 ppm. The plus-point for this concept is that the treated natural gas feed is pre-cooled at -88°C before entering natural gas liquefaction. Another great success in cryogenic-concept distillation method is Controlled Freeze Zone™ (CFZ) (B.T. Kelly, 2011).The technology was demonstrated through pilot plant by

ExxonMobil. Presently, they are upgrading the technology-driven method to large scale in USA. The main component in CFZ consist of single step separation CO_2 and H_2S from natural gas involving the controlled freezing and re-melting of CO_2 in the specially designed chamber. The three-phase separation will resulted in high purity of methane. One of the interesting fact using CFZ is that it avoid solidification of CO_2 that can resulted in dry gas precipitation in pipeline.

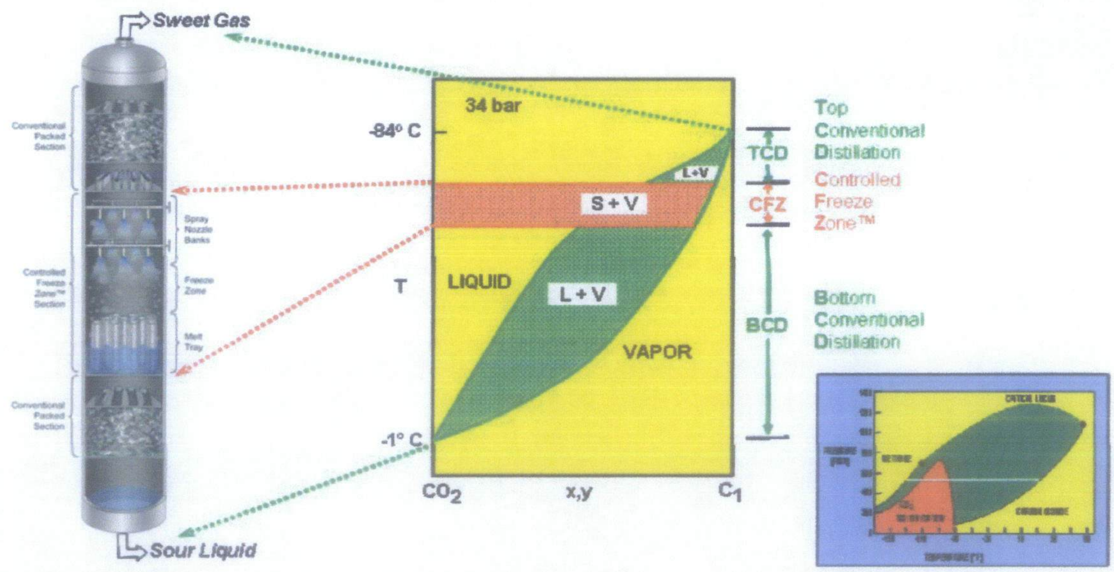

Figure 1: Controlled Freeze Zone Process

In previous work, Tuinier et. al.(2009) developed a novel cryogenic CO_2 capture process from flue gas using dynamically operated packed beds. The main concept in the study were using three cycles, namely (i) cooling cycle (ii) capture cycle and (iii) removal cycle. The bed temperature initially was brought down below the freezing point of CO_2. The flue gases were then introduced to the bed, to capture CO_2 in the gas stream. At standard temperature and pressure (STP) separation of CO_2, H_2O and permanent gases can be done. As the freezing point of permanent gases are much lower than CO_2 and H_2O, it will pass through the bed without any physical change, while both components sublimate onto the surface of the packing. As results, 99% of CO_2 can be recovered from flue gas comprises of 10 vol% of CO_2 and 1 vol.% of H_2O. The advantage of disclosed process is recovering H_2O and CO_2 simultaneously without any plugging. But, it was completed in batch process and low CO_2 content in flue gas.

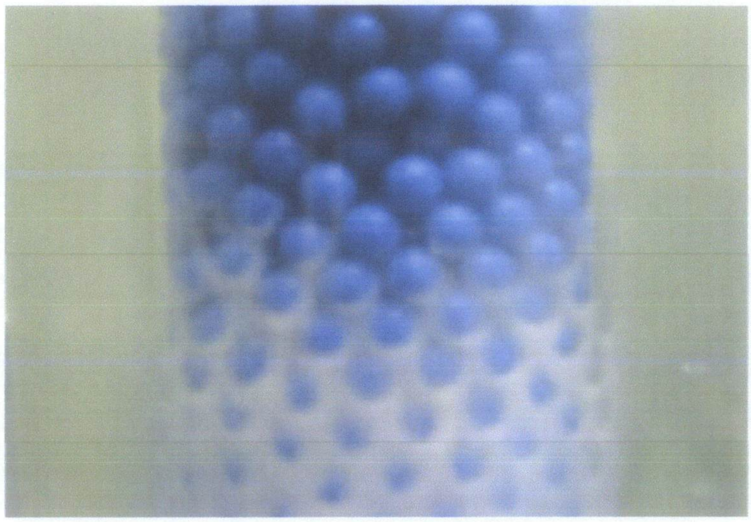

Figure 2: Solid CO_2 deposited at the packing surface during capture cycle (Tuinier et. al. 2009)

Hassan, Syahera and Ganguly (2012) studied cryogenic separation from natural gas experimentally. They used high concentration of CO_2 in the feed stream to observe the effectiveness of cryogenic packed bed in capturing CO_2 in CH_4-CO_2 mixture. The methodology used in this study is based on the principle of desublimation of component onto the surface of the packing. 1-Dimensional Pseudo Homogenous model were used to numerically study the behavior of individual component, mass and energy balance for the system (Ali, Ganguly & Shariff, 2013)

Consequently, the team developed experimental setup using multiple cryogenic packed bed for separation of water and CO_2 from natural gas. The separation principle of water and CO_2 from natural gas is the difference in freezing point of individual component. The desublimation of water and CO_2 from natural gas is described using 1-Dimensional Pseudo Homogenous model. Figure below illustrated the schematics of multiple bed cryogenic separation (Ali, et. al. 2013).

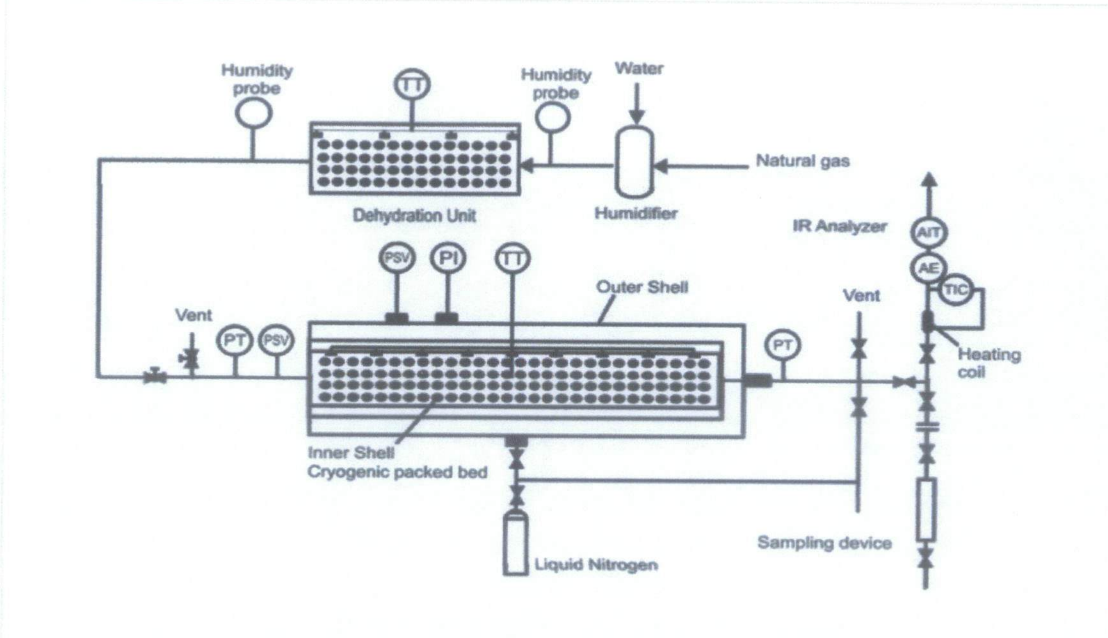

Figure 3: Schematic Diagram of Multiple Bed Cryogenic Separation

2.2 Natural Gas Dehydration

Water must be removed from natural gas stream prior to distribution line in order to prevent pipeline wall corrosion and formation of hydrates and ice (Wen, 2011). Water vapor also potential to reduction in line capacity due to its content. The process of removing water from natural gas stream is called dehydration. Water is condensed by bringing the stream temperature below freezing point of water. There are number of methods for dehydration of natural gas purposes such as absorption using triethylene glycol (TEG),adsorption on solid desiccants as well as condensation (Netusil, 2011).

Absorption process using triethylene glycol separates water from natural gas in tray column or packed bed. TEG absorbs water from the wet gas then suspended at the bottom of the column where they are removed. Consequently, dry natural gas drained out of the top of the column. During condensation, water molecules turn to liquid and then removes them from the steam. When the temperature of the bed falls below freezing point of water, phase change occur and water is stripped out of the system.

On the other hand, for adsorption for solid desiccant does not involves any chemical reaction, unlike absorption. It mainly a surface phenomenon, where water vapor are held on the surface of solid. From industrial point of view, water must be removed to meet allowable water content in sales gas, ranging from 32.8 to 117 kg water/ 10^6 std m^3 of gas (Gandhidasan, 2000).

2.3 Methane-CO_2 mixture

The most important details to be reviewed is the composition of CO_2 and methane in Malaysia's natural gas reserve. All experimental and simulation study will revolve around this data as it will determine the main process for our separation technology. The thermodynamic data for CO_2 is crucial as we will figure out the best parameter to treat the natural gas.

The first literature to be reviewed is by Ozturk (2010). He came out with many sets of data from his modeling using PC-SAFT equation of state. Perturbed- Chain Statistical Associating Fluid Theory or PC-SAFT is state-of-the-art, engineering-like equation of state. It is suitably designed for the calculation of phase equilibria and thermophysical properties of pure components and mixtures. He reviewed the available data and provided a predictive model that characterize data over the whole sets of temperatures and pressure for solid-liquid-vapor equilibria. He was then connected all the data to PC-SAFT at very low temperature and high pressures.

One of his work that is related to the cryogenic topic is the liquid composition which separates CO_2 completely from methane at high pressure stream. He compared his model with previous available data.

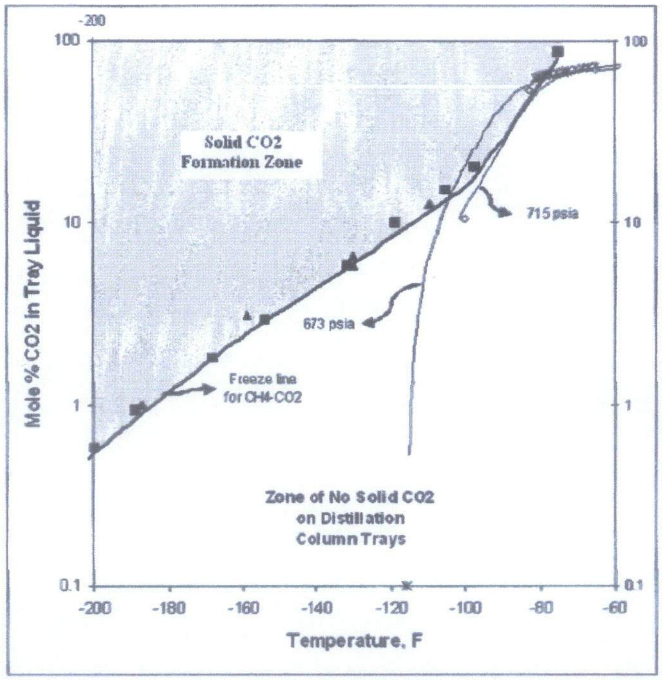

Figure 4: Mole Percent of CO2-Pressure diagram for Solid-Liquid Equilibria

The figure is taken from operating the natural gas stream through cryogenic distillation at 715 psia and 673 psia. The shaded area represent solid CO_2 formation while white area showed properties of no CO_2 solid will occur. The data is very useful in determining the operating parameters of the distillation to separate CO_2 from methane. The model also indicate that PC-SAFT accurately parallel with previous data available.

He added that there are irregularities between past data regarding methane and CO_2 solid-liquid equilibrium. Some of them deviate after -100 F and exhibit an eutectic for methane and CO_2. On the other hand, another set of data show no sign of eutectic for the system.

In determining the solidification of solid carbon dioxide in the methane-CO_2 binary system, there are two methods (Lavik, 2009). The first one is the carbon dioxide content in a liquid exceeds the solubility limit of the liquid phase which is indicated by the freezing line (DE). This can be achieved by super cooling of the liquid phase. On the other hand, if the carbon dioxide content exceeds the solubility limit of the gas phase, the CO_2 will solidify. This is more to solid-vapor equilibrium, which is indicated by AB line.

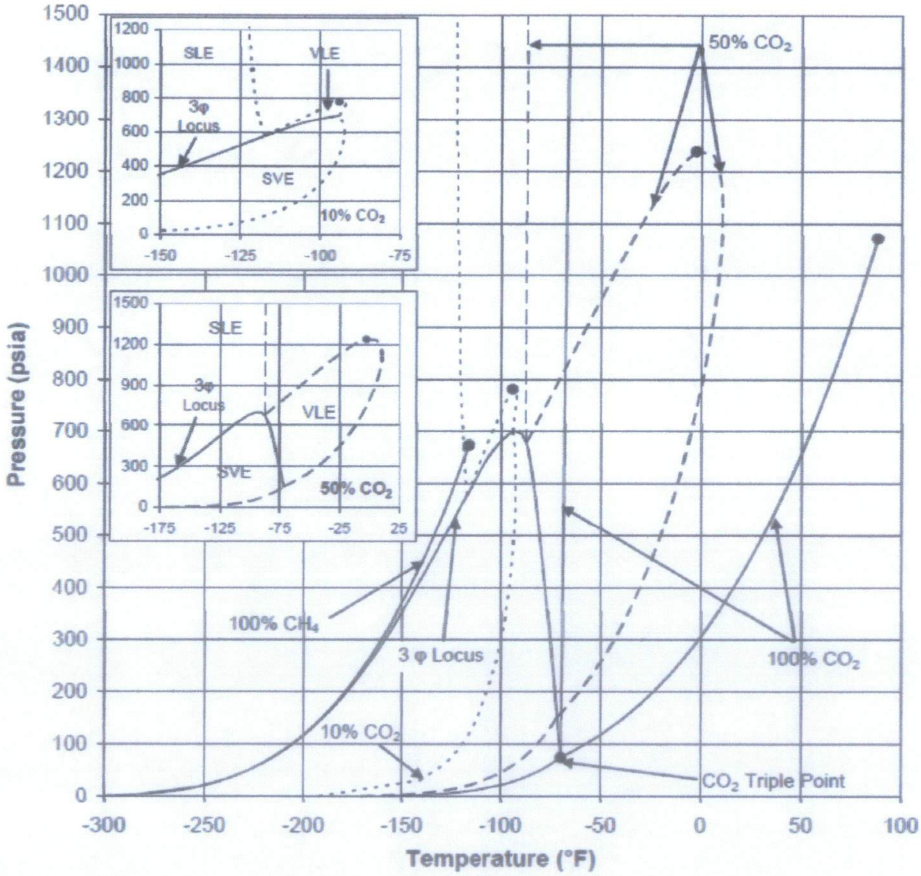

Figure 5: Pressure-Temperature Diagram for the 0%, 10%, 50%, and 100% Carbon Dioxide in Methane Binary System.

In separation of acidic gas from natural gas stream, one of the important data is freezing point for CO_2. This will determine the operating condition (e.g. Pressure, Temperature) for the separator. Thus, simulation and experimental data can provide sufficient information for the optimization of separation of natural gas.

In order to predict precisely the characteristic of different thermodynamic values, few computer programs can be used to predict the freeze out of different components in natural gas mixtures (Lavik, 2009). Some of the common modeling software are

NEQSIM, a simulation model that provides the tools to implement algorithm for modeling and calculating phase equilibrium and also GERG 2008. On the other hand. HYSYS can also be used to calculate the solid-liquid equilibrium. HYSYS offers traditional Peng- Robinson and Soave- Redlich- Kwong equations of state and the level of complexity is much higher.

CHAPTER 3

METHODOLOGY

3.1 Cryogenic Packed Bed

In this study, cryogenic packed bed is used to separate water (H_2O) and carbon dioxide (CO_2) from natural gas stream. Cryogenic packed bed utilizes the concept of freezing point of each component in natural gas. When the stream of natural gas pass through the cryogenic bed, the component which has higher freezing point will desublimate onto the surface of the packing. The lower freezing point will retain in gaseous form.

Since the processing methods of natural gas came from continuous feed, the cryogenic packed bed must be able to be operated in continuous process as well. Thus, multiple cryogenic packed bed is proposed to be further studied in this project. The separation of H_2O and CO_2 will thoroughly optimized and experimented to determine the best operating condition for the packed bed. Different packed bed will operate at different operating condition, depending on its purpose.

The removal of water must be conducted prior to CO_2 separation process as water tends to form hydrates at low temperature with other component and consequently cause plugging and inner pipe's corrosion. At atmospheric pressure, water will solidify at $0^{o}C$. The allowable water content in natural gas processing pipeline is 1 ppm weight. Next, the removal of CO_2 is done in separate bed. At standard temperature and pressure (STP) CO_2 change it phase from gas to solid at $-78^{o}C$. This type of phase change is called anti-sublimation or desublimation.

The main idea behind separation at low temperature consist of three cycles. The first cycle is cooling cycle, where the packed bed is cooled to the desired temperature. Secondly, feed gas, which is the natural gas in passed through the bed and the component start to desublimate onto the surface of the packing. In the last cycle, recovery cycle, frost component are recovered. The proposed schematic diagram of the cryogenic packed bed network is shown in the Figure 6. Table 2 indicates the composition of natural gas used in the study (Engineer, 2004).

Table 2: Composition of Natural Gas

Pressure	80.00 bar
Temp	25 °C
CH_4	0.440
C_2H_6	0.050
C_3H_8	0.027
i-C_4H_{10}	0.010
n-C_4H_{10}	0.010
i-C_5H_{12}	0.010
n- C_5H_{12}	0.001
C_6H_{14}	0.001
C_7H_{16}	0.001
C_8H_{18}	0.001
H2O	0.040
CO_2	0.400
N2	0.010

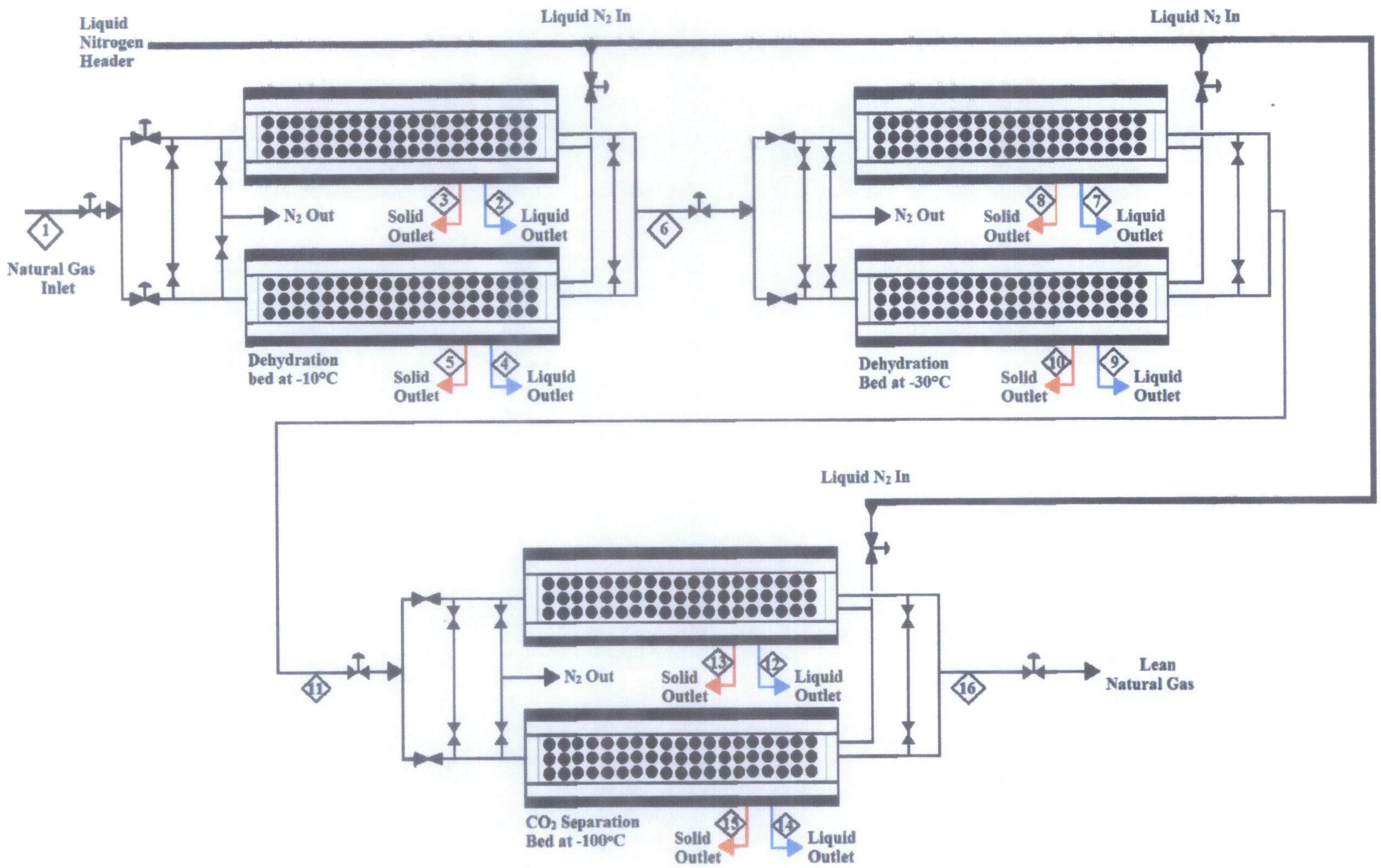

Figure 6: Proposed Schematic Diagram of Cryogenic Packed Bed Network

3.2 Statistical Optimization

High pressure stream from natural gas field are fed to natural gas processing facilities on the offshore facilities to sweeten the natural gas. The impurities contain in the natural gas are mainly H_2O and CO_2. Since the proposed technology is by using cryogenic packed bed, water must be removed prior to CO_2 due to tendency of water to form hydrates with other hydrocarbons or even CO_2.

From thermodynamic point of value, each component behave differently when they are mix together and operated at high pressure as compared to its situation at atmospheric pressure. ASPEN Hysys® are used to study the separation of water as well as CO_2 from natural gas. Peng-Robinson package is used to observe the behavior of the natural gas processing at low temperature. A set of temperature and pressure are elevated accordingly to optimize the best operating condition for cryogenic packed bed. The criteria for selection of optimization of cryogenic packed bed are as follows:

i. Maximum Separation of H_2O and $CO_2$from natural gas
ii. Minimum hydrocarbon loss
iii. Minimum pressure drop between the beds

3.3 Experimental Setup

Dehydration

In the first experiment, water removal is studied to observe the effectiveness of the packed bed towards dehydration process. The temperature are ranging from 0°C to -10°C. The temperature of the bed is easily obtained using salted ice. Once the temperature are still at -10°C, mixture of gases are passed through the bed and water will be removed and frost on the surface of the packing.

In the next experiment, water removal from gas stream is conducted at -30°C. For the experiment, liquid nitrogen is used to bring down the temperature of the bed to -30°C. Both experiment are conducted to observe the performance of the bed to remove water at low temperature. The schematic diagram of cryogenic packed bed and experimental setup for H_2O removal are shown below.

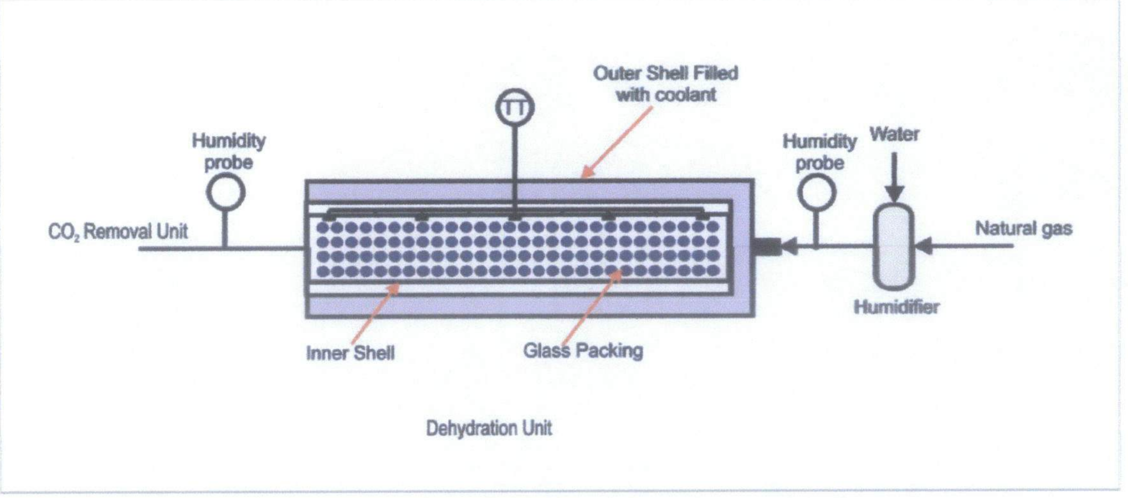

Figure 7: Schematic Diagram for Cryogenic Packed Bed for Water Removal

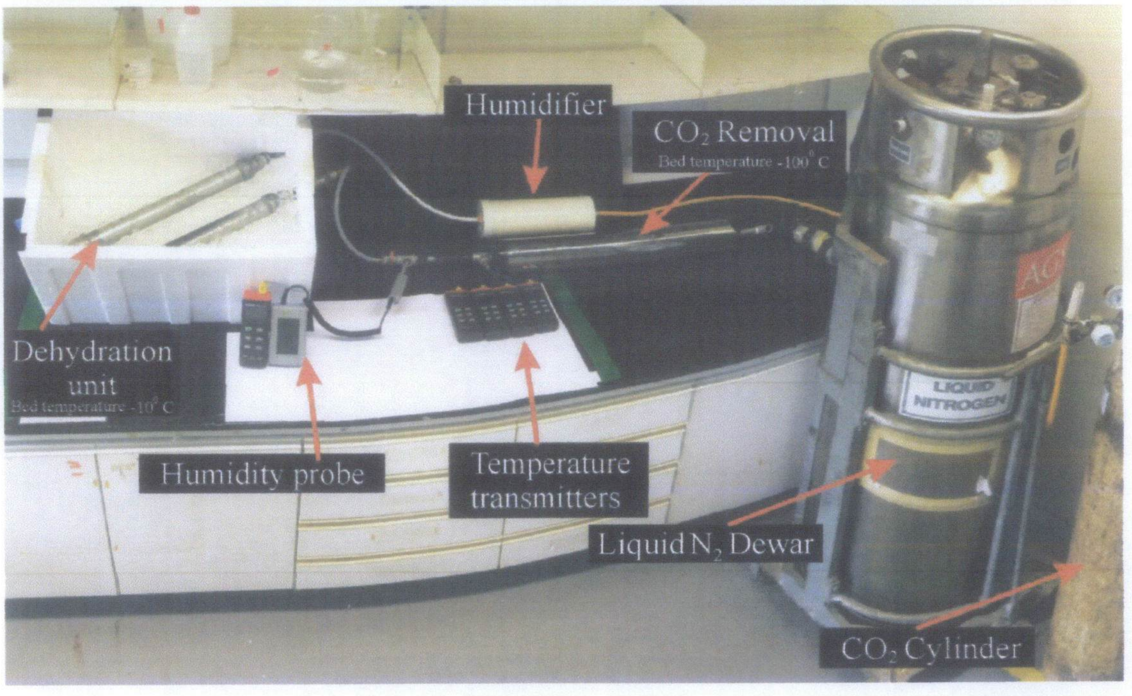

Figure 8: Experimental Setup for Dehydration (-10°C) and CO_2 removal (-100°C)

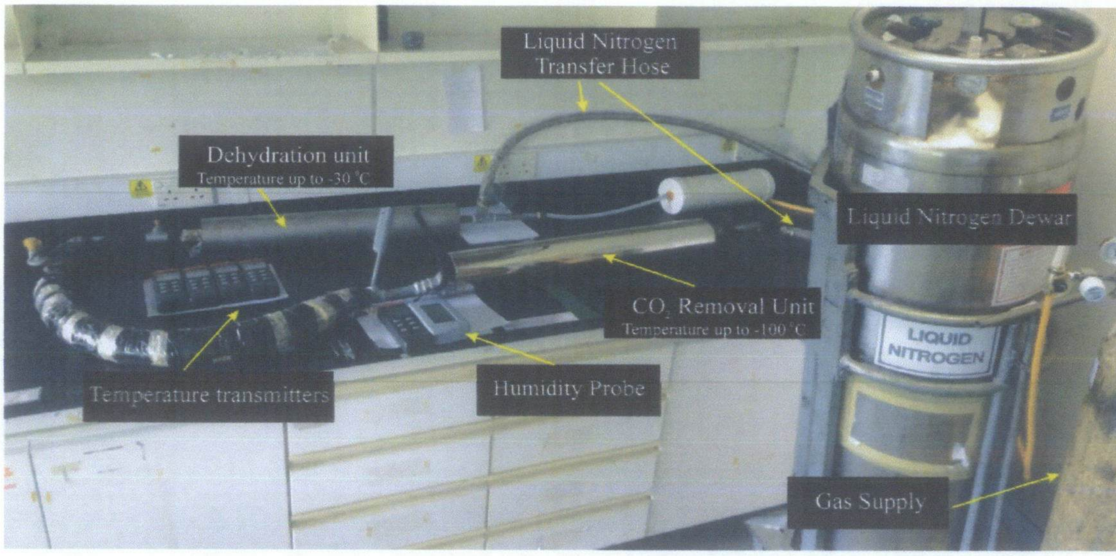

Figure 9: Experimental Setup for Dehydration (-30°C) and CO2 removal(-100°C)

CO_2 Capture Using Cryogenic Packed Bed

The separation of natural gas are based on the difference in freezing point of the components. Cryogenic packed bed is first cooled to temperature ranging from -80°C to -100°C. Then, the natural gas is passed through the packed bed in capture cycle. Liquid nitrogen is used to bring the temperature of the bed down to -100°C. The schematic diagram of the packed bed is shown as below:

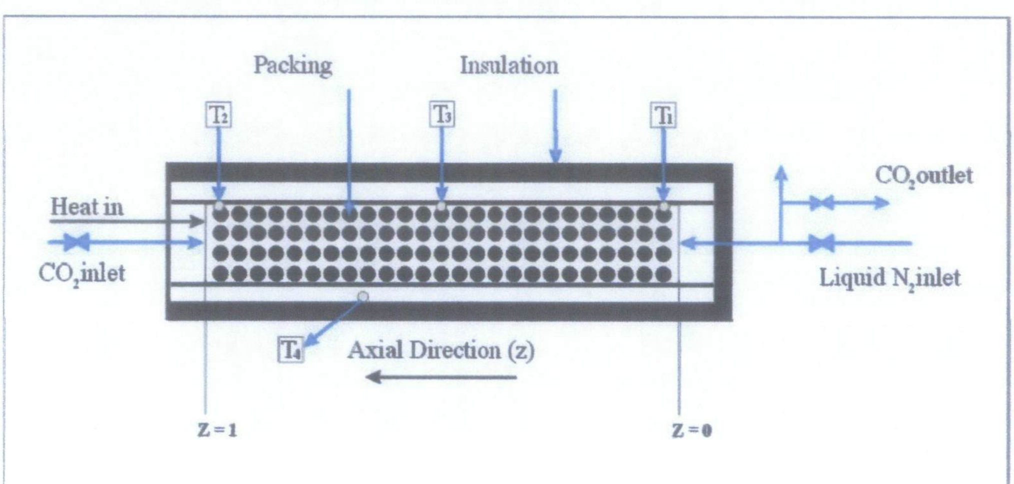

Figure 10: Schematic Diagram of Cryogenic Packed Bed for CO_2 Removal

The bed was constructed to remove water and CO_2 from natural gas stream. Stainless steel pipe were used as the shell for the packed bed and glass marble are used as packing inside the shell. 2 inch insulation are used to minimize heat loss towards surrounding. Several thermocouple were used to investigate the temperature change within the bed during experimentation. Gas feeding system are comprised of multiple inlet of different pure gases from gas cylinder. The physical properties of the packed bed are illustrated as per below.

Table 3: Physical Properties of Cryogenic Packed Bed

Bed Properties	
Length	1.02
Diameter	0.0418 m
Porosity	0.64
Packing Properties	
Mass	2.5 kg
Density	2000 kg/m^3
Diameter	0.01 m
Heat Capatcity	0.466 J/kg·K

3.3 Technical Gantt Chart

Table 4: Technical Gantt Chart for Final Year Project (FYP)

		FYP 1								FYP 2							
No.	Detail/ Week	1-2	3-4	5-6	7-8	9-10	11-12	13-14	Semester Break	1-2	3-4	5-6	7-8	9-10	11-12	13-14	15
1	Problem Understanding & Objectives Identification																
2	Literature Revision																
3	Statistical Optimization of Cryogenic Separation at Different Temperature and Pressure																
4	Developing temperature profile for each packed bed																
5	Dehydration Process Experiment																
6	CO_2Removal Experiment																
7	Results Collection and analysis																
8	Process optimization																
9	Presentation and Documentation																

CHAPTER 4

RESULT AND DISCUSSION

4.1 Statistical Optimization – High Pressure

The statistical optimization of cryogenic packed bed operation at high pressure has been identified. As a result, 5 sets of cryogenic packed beds are needed to separate water and CO_2 from natural gas stream. 2 sets of dehydration beds are required to maximize dehydration process and 3 sets of cryogenic packed beds for CO_2 removal are used to sweeten the natural gas. The block diagram for cryogenic packed beds operation is shown in Figure 12.

Dehydration Bed 1 & 2

The first two cryogenic packed beds are operated to remove water from the feed gas. Initially, the water content inside natural gas are 40 kmol/hr, which is comprised of 4% of natural gas composition. The first bed removes most of the water as compared to the second bed. The bed's pressure are maintain at 80 bar as per feed pressure. The water solidifies at $0^{\circ}C$ regardless of pressure of the stream. This is determined by the thermodynamic properties of water.

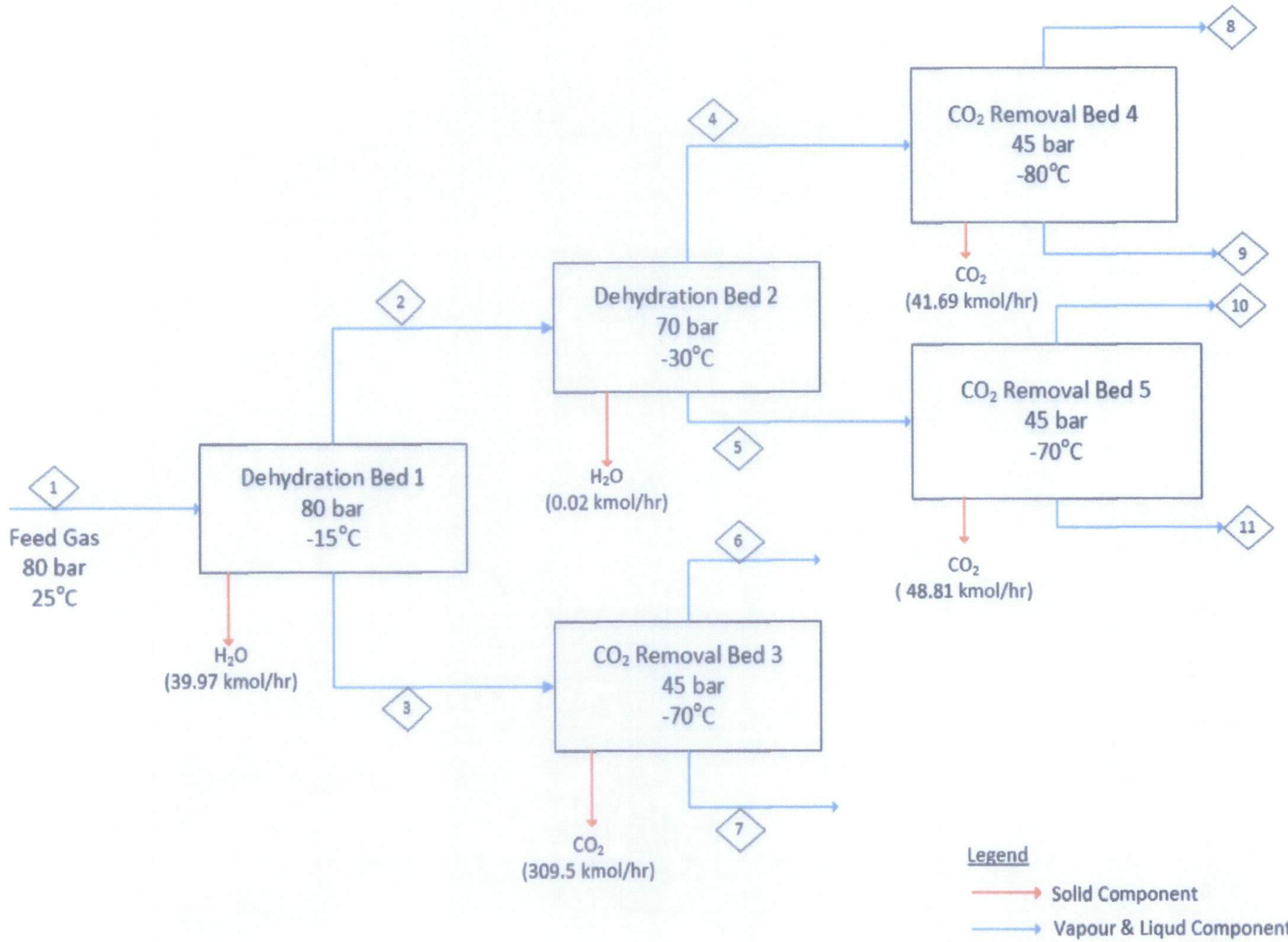

Figure 11: Block Diagram for Multiple Cryogenic Packed Bed Networks at High Pressure

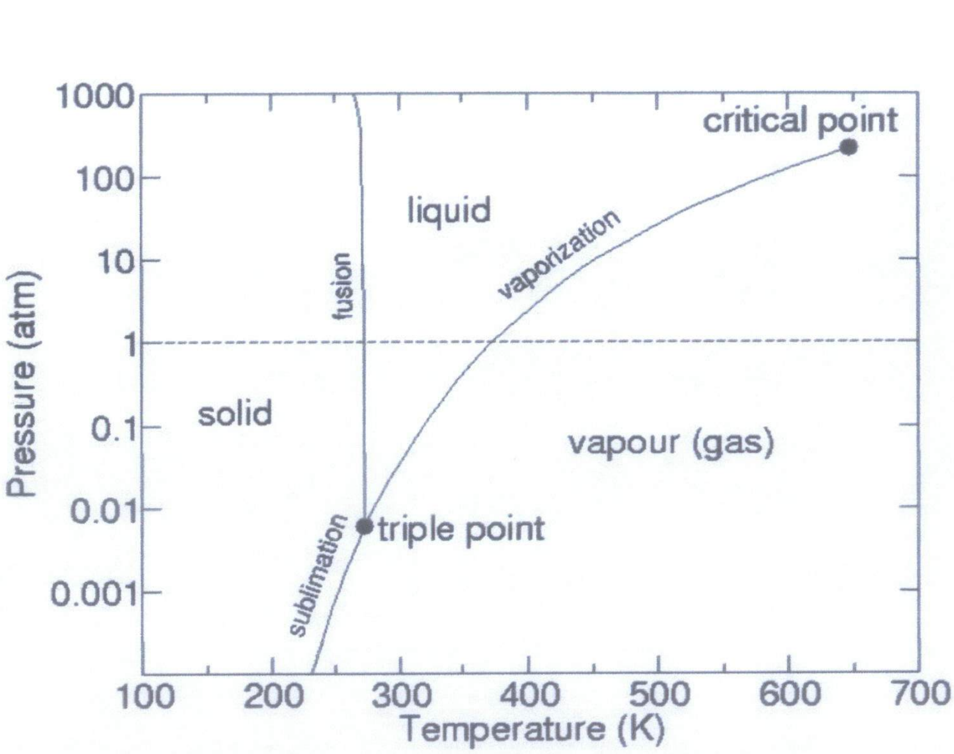

Figure 12: Phase Diagram of Water

-15°C are taken to maximize water frosting inside the bed. Temperature less than -15°C will reduce CH_4 in the gas stream while the temperature above -15°C will results in less water separated from the stream. Table 5 illustrated the separation of component becoming gas and liquid at different temperature and pressure for dehydration bed 1.

Top product of the first bed become the feed for 2nd dehydration process to further remove the water. Since most of the water has been removed in the first bed, the second bed optimal condition is chosen at 70 bar and -30°C. The maximum separation of water is at -30°C for each temperature. For 80 bar, water is removed completely from the stream but the amount of CH_4 in the vapor stream is minimal. So without losing much pressure in the stream, most of the water left in the vapor stream from the first bed is removed in the second one at 70 bar and keep the CH_4 in the vapor form. The minimum loss of hydrocarbon is achieved from the optimal condition as compared to 80 bar and -30°C. The effect of temperature and pressure elevation towards separation of components on Dehydration Bed 2 are shown in Table 6.

Table 5: Effect of Temperature and Pressure Elevation Towards Separation of Component on Dehydration Bed 1

	Feed	Gas																			
Pressure (bar)	80.00	80.00						70.00							60.00						
Temp (°C)	25.00	0.00	-2.00	-5.00	-10.00	-15.00	-20.00	0.00	-2.00	-5.00	-10.00	-15.00	-20.00	-30.00	0.00	-2.00	-5.00	-10.00	-15.00	-20.00	-30.00
CH_4	440.000	385.90	367.38	332.19	252.82	145.50	1.52	408.43	399.10	381.27	340.67	287.06	220.54	40.06	423.08	418.61	409.83	388.16	356.78	315.58	211.23
C_2H_6	50.000	39.34	36.38	31.26	21.49	11.01	0.10	41.79	39.79	36.25	29.30	21.86	14.59	1.93	44.32	43.02	40.63	35.42	29.11	22.59	11.08
C_3H_8	27.000	18.77	16.91	13.93	8.91	4.27	0.04	19.45	17.97	15.58	11.50	7.83	4.83	0.57	20.77	19.60	17.62	13.93	10.26	7.15	2.92
i-C_4H_{10}	10.000	6.17	5.45	4.35	2.66	1.23	0.01	6.12	5.51	4.59	3.17	2.04	1.20	0.13	6.44	5.90	5.07	3.70	2.53	1.65	0.61
n-C_4H_{10}	10.000	5.83	5.10	4.03	2.42	1.10	0.01	5.63	5.01	4.11	2.77	1.74	1.01	0.11	5.85	5.30	4.46	3.15	2.09	1.33	0.48
i-C_5H_{12}	10.000	4.97	4.27	3.28	1.90	0.84	0.01	4.42	3.83	3.02	1.94	1.17	0.66	0.07	4.34	3.81	3.06	2.03	1.27	0.78	0.26
n-C_5H_{12}	1.000	0.47	0.40	0.30	0.17	0.08	0.00	0.40	0.34	0.27	0.17	0.10	0.06	0.01	0.38	0.33	0.26	0.17	0.11	0.06	0.02
C_6H_{14}	1.000	0.35	0.30	0.22	0.12	0.05	0.00	0.26	0.22	0.17	0.10	0.06	0.03	0.00	0.22	0.19	0.14	0.09	0.05	0.03	0.01
C_7H_{16}	0.500	0.13	0.11	0.08	0.04	0.02	0.00	0.08	0.07	0.05	0.03	0.02	0.01	0.00	0.06	0.05	0.04	0.02	0.01	0.01	0.00
C_8H_{18}	0.500	0.10	0.08	0.06	0.03	0.01	0.00	0.05	0.04	0.03	0.02	0.01	0.00	0.00	0.03	0.02	0.02	0.01	0.01	0.00	0.00
H2O	40.000	0.23	0.19	0.14	0.07	0.03	0.00	0.21	0.18	0.14	0.08	0.05	0.02	0.00	0.21	0.18	0.15	0.09	0.05	0.03	0.01
CO_2	400.000	321.44	297.96	256.69	176.75	90.50	0.83	344.18	328.75	300.71	243.65	181.35	121.24	16.27	365.50	356.34	338.60	297.09	243.94	187.89	90.50
N2	10.000	9.13	8.81	8.15	6.53	4.04	0.05	9.58	9.44	9.17	8.51	7.55	5.23	1.40	9.81	9.75	9.64	9.35	8.91	8.29	6.37

		Liquid																			
Pressure (bar)	80.00	80.00						70.00							60.00						
Temp (°C)	25.00	0.00	-2.00	-5.00	-10.00	-15.00	-20.00	0.00	-2.00	-5.00	-10.00	-15.00	-20.00	-30.00	0.00	-2.00	-5.00	-10.00	-15.00	-20.00	-30.00
CH_4		54.10	72.62	107.81	187.18	294.50	438.48	31.57	40.90	58.73	99.33	152.94	219.06	399.94	16.92	21.39	30.17	51.84	83.22	123.42	228.77
C_2H_6		10.66	13.62	18.74	28.51	38.99	49.90	8.21	10.21	13.75	20.70	28.14	35.31	48.02	5.68	6.98	9.37	14.58	20.89	27.41	38.92
C_3H_8		8.23	10.09	13.07	18.09	22.73	25.96	7.55	9.03	11.42	15.50	19.17	22.17	26.43	6.23	7.40	9.38	13.07	16.74	19.85	24.08
i-C_4H_{10}		3.33	4.55	5.65	7.34	8.77	9.99	3.88	4.49	5.41	6.83	7.96	8.60	9.87	3.56	4.10	4.93	6.30	7.47	8.35	9.39
n-C_4H_{10}		4.17	4.90	5.97	7.58	8.90	9.99	4.37	4.99	5.89	7.23	8.26	8.99	9.89	4.15	4.70	5.54	6.85	7.91	8.67	9.52
i-C_5H_{12}		5.03	5.73	6.72	8.10	9.16	9.99	5.58	6.17	6.98	8.06	8.83	9.34	9.93	5.66	6.19	6.94	7.97	8.73	9.22	9.74
n-C_5H_{12}		0.53	0.60	0.70	0.83	0.92	1.00	0.60	0.66	0.73	0.83	0.90	0.94	0.99	0.62	0.67	0.74	0.83	0.89	0.94	0.98
C_6H_{14}		0.64	0.70	0.78	0.88	0.95	1.00	0.74	0.78	0.83	0.90	0.94	0.97	1.00	0.78	0.81	0.86	0.91	0.95	0.97	0.99
C_7H_{16}		0.37	0.39	0.42	0.46	0.48	0.50	0.42	0.43	0.45	0.47	0.48	0.49	0.50	0.44	0.45	0.46	0.48	0.49	0.49	0.50
C_8H_{18}		0.40	0.42	0.44	0.47	0.49	0.50	0.45	0.46	0.47	0.48	0.49	0.50	0.50	0.47	0.48	0.48	0.49	0.49	0.50	0.50
H20		39.77	39.81	39.86	39.93	39.97	40.00	39.79	39.82	39.86	39.92	39.95	39.98	40.00	39.79	39.82	39.85	39.91	39.94	39.97	39.99
CO2		78.56	102.04	143.31	223.25	309.50	399.17	55.82	71.24	99.29	156.35	218.65	278.76	383.73	34.50	43.66	61.40	102.91	156.06	212.11	309.50
N2		0.37	1.19	1.85	3.47	5.96	9.95	0.42	0.56	0.83	1.49	2.45	3.77	8.60	0.19	0.25	0.36	0.65	1.09	1.71	3.63

Table 6: Effect of Temperature and Pressure Elevation Towards Separation of Components on Dehydration Bed 2

	Feed	Gas											
Pressure (bar)	80.00	80.00			70.00			60.00			50.00		
Temp (°C)	-15.00	-20.00	-25.00	-30.00	-20.00	-25.00	-30.00	-20.00	-25.00	-30.00	-20.00	-25.00	-30.00
CH_4	145.50	126.76	88.76	0.00	132.89	117.61	96.73	139.58	131.34	119.92	143.42	139.67	133.20
C_2H_6	11.01	8.90	5.69	0.00	8.98	7.08	5.09	9.72	8.24	6.59	10.39	9.44	8.04
C_3H_8	4.27	3.20	1.91	0.00	3.00	2.10	1.36	3.27	2.41	1.68	3.66	2.94	2.13
I C_4H_{10}	1.23	0.86	0.49	0.00	0.73	0.47	0.28	0.79	0.51	0.32	0.91	0.63	0.40
n C_4H_{10}	1.10	0.75	0.42	0.00	0.61	0.37	0.22	0.64	0.39	0.24	0.75	0.48	0.29
i-C_5H_{12}	0.84	0.52	0.28	0.00	0.37	0.21	0.12	0.36	0.20	0.11	0.42	0.23	0.12
n- C_5H_{12}	0.08	0.05	0.02	0.00	0.03	0.02	0.01	0.03	0.02	0.01	0.03	0.02	0.01
C_6H_{14}	0.05	0.03	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.00
C_7H_{16}	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_8H_{18}	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H2O	0.03	0.02	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.00
CO_2	90.50	73.36	46.86	0.00	74.33	58.33	41.69	80.76	68.17	53.76	86.51	78.84	66.25
N2	4.04	3.62	2.66	0.00	3.81	3.51	3.05	3.95	3.81	3.62	4.01	3.96	3.87

	Feed	Liquid											
Pressure (bar)	80.00	80.00			70.00			60.00			50.00		
Temp (°C)	-15.00	-20.00	-25.00	-30.00	-20.00	-25.00	-30.00	-20.00	-25.00	-30.00	-20.00	-25.00	-30.00
CH_4		18.74	56.74	145.50	12.61	27.89	48.77	5.92	14.17	25.58	2.09	5.83	12.30
C_2H_6		2.11	5.33	11.01	2.03	3.93	5.93	1.30	2.77	4.42	0.62	1.57	2.97
C_3H_8		1.07	2.36	4.27	1.28	2.17	2.91	1.01	1.86	2.59	0.61	1.34	2.15
i-C_4H_{10}		0.37	0.74	1.23	0.49	0.76	0.94	0.44	0.72	0.91	0.32	0.60	0.83
n-C_4H_{10}		0.36	0.69	1.10	0.49	0.73	0.88	0.46	0.71	0.86	0.35	0.62	0.81
I C_5H_{12}		0.32	0.56	0.84	0.48	0.64	0.73	0.48	0.65	0.73	0.42	0.61	0.72
n C_5H_{12}		0.03	0.05	0.08	0.05	0.06	0.07	0.05	0.06	0.07	0.04	0.06	0.07
C_6H_{14}		0.03	0.04	0.05	0.04	0.05	0.05	0.04	0.05	0.05	0.04	0.05	0.05
C_7H_{16}		0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
C_8H_{18}		0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
H2O		0.01	0.02	0.03	0.01	0.02	0.02	0.01	0.02	0.02	0.01	0.02	0.02
CO_2		17.14	48.68	90.50	16.17	32.17	48.81	9.73	22.33	36.73	3.99	11.66	24.25
N2		0.41	1.38	4.04	0.22	0.52	0.98	0.09	0.22	0.42	0.03	0.08	0.17

CO_2 Removal Bed 3, 4 and 5

For these beds, the purpose is to frost CO_2 to be separated completely from the natural gas. As for CO_2 removal unit, the maximum operating pressure for cryogenic packed bed is at 45 bar. This is because from thermodynamic point of view, methane is at supercritical condition above 45 bar (ZareNezhad, 2006). Hence, the separation of CO_2 and methane will not be effective in the supercritical region. The diagram below show the critical region for CH_4.

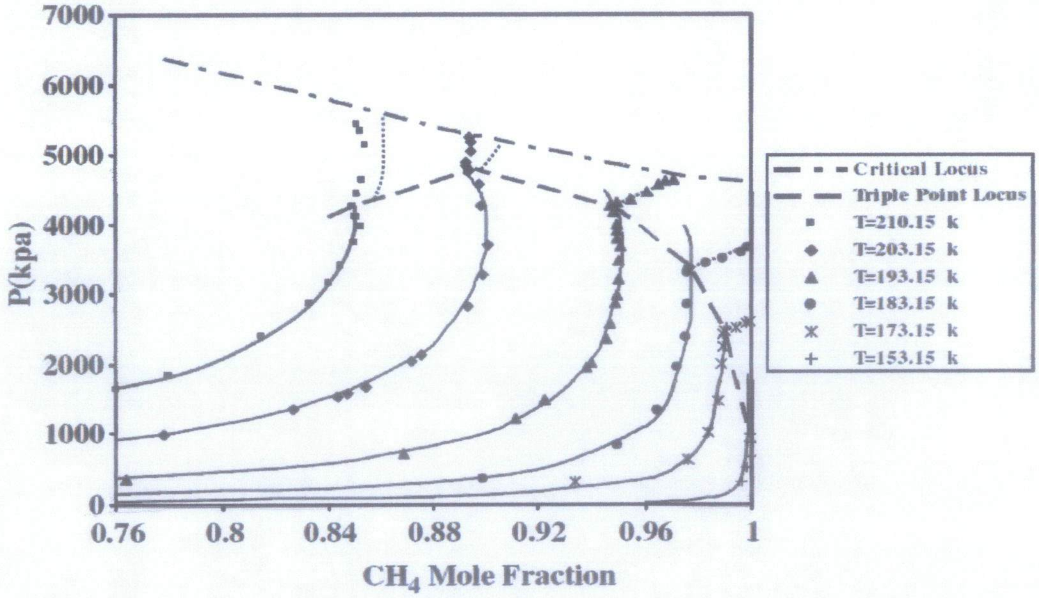

Figure 13: CO2 Freezing Points for CO2–CH4 vapor mixtures

The bottom product of the first bed are fed to the third bed knowingly CO_2 removal bed 3. According to the table below, CO_2 solidified at -70°C and lower for all the pressure in the 3rd. As results, both product from this bed are lean natural gas as CO_2 desublimate onto the surface of the packing in the CO_2 removal bed.

For Bed 4, the temperature for operating condition is chosen at -80°C. This is because the solidification temperature of CO_2 is at -71.10°C. The value is calculated by the simulator. Meanwhile for Bed 5, the solidification temperature of CO_2 in the mixture is at 69.02°C. So -70°C is chosen for the bed to be operated.

The difference in temperature for all three beds for CO_2 removal unit is mainly due to freezing point of CO_2. At the same pressure, the freezing point of CO_2 is influenced by the composition of CO_2 in the stream (Harold G. Donnelly, 1954).

Table 7: Effect of Temperature and Pressure Elevation Towards Separation of Components on CO_2 Removal Bed 3

	Feed	Gas																
Pressure (bar)	80.00	45.00				40.00				30.00				20.00				
Temp (°C)	-15.00	-50.00	-60.00	-70.00	-80.00	-50.00	-60.00	-70.00	-80.00	-50.00	-60.00	-70.00	-80.00	-50.00	-60.00	-70.00	-80.00	-90.00
CH_4	294.50	65.59	0.00	0.00	0.00	121.50	27.24	0.00	0.00	203.16	152.61	74.31	0.00	258.85	231.56	196.33	142.95	44.03
C_2H_6	38.99	1.99	0.00	0.00	0.00	4.10	0.60	0.00	0.00	9.10	4.46	1.34	0.00	17.57	10.41	5.62	2.43	0.40
C_3H_8	22.73	0.36	0.00	0.00	0.00	0.71	0.09	0.00	0.00	1.54	0.62	0.16	0.00	3.30	1.48	0.64	0.23	0.03
i-C_4H_{10}	8.77	0.06	0.00	0.00	0.00	0.11	0.01	0.00	0.00	0.22	0.08	0.02	0.00	0.46	0.18	0.07	0.02	0.00
n-C_4H_{10}	8.90	0.04	0.00	0.00	0.00	0.08	0.01	0.00	0.00	0.14	0.05	0.01	0.00	0.29	0.11	0.04	0.01	0.00
i-C_5H_{12}	9.16	0.02	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.05	0.02	0.00	0.00	0.10	0.04	0.01	0.00	0.00
n- C_5H_{12}	0.92	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
C_6H_{14}	0.95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_7H_{16}	0.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_8H_{18}	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO_2	309.50	15.84	0.00	0.00	0.00	31.86	4.71	0.00	0.00	68.94	32.49	9.88	0.00	139.81	73.61	36.70	15.56	2.77
N2	5.96	2.46	0.00	0.00	0.00	3.86	1.29	0.00	0.00	5.17	4.58	3.12	0.00	5.72	5.53	5.25	4.70	2.57

	Feed	Liquid																
Pressure (bar)	80.00	45.00				40.00				30.00				20.00				
Temp (°C)	-15.00	-50.00	-60.00	-70.00	-80.00	-50.00	-60.00	-70.00	-80.00	-50.00	-60.00	-70.00	-80.00	-50.00	-60.00	-70.00	-80.00	-90.00
CH_4		228.91	294.50	294.50	294.50	173.00	267.26	294.50	294.50	91.34	141.89	220.19	294.50	35.65	62.94	98.17	151.55	250.46
C_2H_6		36.99	38.99	38.99	38.99	34.88	38.39	38.99	38.99	29.88	34.52	37.65	38.99	21.42	28.58	33.37	36.56	38.59
C_3H_8		22.37	22.73	22.73	22.73	22.02	22.64	22.73	22.73	21.19	22.10	22.57	22.73	19.43	21.25	22.09	22.50	22.70
i-C_4H_{10}		8.71	8.77	8.77	8.77	8.66	8.76	8.77	8.77	8.55	8.69	8.75	8.77	8.32	8.59	8.70	8.75	8.77
n-C_4H_{10}		8.86	8.90	8.90	8.90	8.82	8.89	8.90	8.90	8.75	8.85	8.89	8.90	8.61	8.79	8.86	8.89	8.90
i-C_5H_{12}		9.14	9.16	9.16	9.16	9.12	9.15	9.16	9.16	9.10	9.14	9.15	9.16	9.06	9.12	9.14	9.15	9.16
n- C_5H_{12}		0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
C_6H_{14}		0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.94	0.95	0.95	0.95	0.95
C_7H_{16}		0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48
C_8H_{18}		0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49
H2O		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO_2		293.66	309.50	309.50	309.50	277.64	304.79	309.50	309.50	240.56	277.01	299.62	309.50	169.69	235.89	272.80	293.94	306.74
N2		3.50	5.96	5.96	5.96	2.11	4.67	5.96	5.96	0.80	1.39	2.84	5.96	0.24	0.44	0.72	1.26	3.39

Table 8: Effect of Temperature and Pressure Elevation Towards Separation of Components on CO_2 Removal Bed 4

	Feed	Gas																		
Pressure (bar)	70.00	45.00				40.00				30.00					20.00					
Temp (°C)	-30.00	-50.00	-60.00	-70.00	-80.00	-50.00	-60.00	-70.00	-80.00	-50.00	-60.00	-70.00	-80.00	-90.00	-60.00	-70.00	-80.00	-90.00	-100.00	-110.00
CH_4	96.73	84.79	68.70	22.41	0.00	88.87	78.40	54.06	0.00	94.29	89.14	81.34	62.92	0.00	94.75	91.43	86.80	77.57	35.09	0.00
C_2H_6	5.09	2.97	1.59	0.28	0.00	3.39	2.07	0.82	0.00	4.31	3.07	1.89	0.79	0.00	4.26	3.15	2.07	1.04	0.15	0.00
C_3H_8	1.36	0.42	0.16	0.02	0.00	0.50	0.21	0.06	0.00	0.79	0.36	0.15	0.05	0.00	0.71	0.33	0.14	0.05	0.00	0.00
$i\text{-}C_4H_{10}$	0.28	0.05	0.02	0.00	0.00	0.06	0.02	0.01	0.00	0.10	0.03	0.01	0.00	0.00	0.08	0.03	0.01	0.00	0.00	0.00
$n\text{-}C_4H_{10}$	0.22	0.03	0.01	0.00	0.00	0.03	0.01	0.00	0.00	0.05	0.02	0.01	0.00	0.00	0.04	0.01	0.00	0.00	0.00	0.00
$i\text{-}C_5H_{12}$	0.12	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
$n\text{-}C_5H_{12}$	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_6H_{14}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_7H_{16}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_8H_{18}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO_2	41.69	22.01	11.75	2.50	0.00	24.98	14.27	6.29	0.00	33.52	19.97	11.17	5.22	0.00	31.10	17.55	9.52	4.74	1.18	0.00
N2	3.05	2.88	2.60	1.26	0.00	2.95	2.80	2.34	0.00	3.03	2.96	2.87	2.61	0.00	3.03	3.00	2.96	2.87	2.17	0.00

	Feed	Liquid																		
Pressure (bar)	70.00	45.00				40.00				30.00					20.00					
Temp (°C)	-30.00	-50.00	-60.00	-70.00	-80.00	-50.00	-60.00	-70.00	-80.00	-50.00	-60.00	-70.00	-80.00	-90.00	-60.00	-70.00	-80.00	-90.00	-100.00	-110.00
CH_4		11.93	28.03	74.32	96.73	7.86	18.33	42.67	96.73	2.44	7.59	15.39	33.81	96.73	1.98	5.30	9.92	19.16	61.64	96.73
C_2H_6		2.11	3.49	4.80	5.09	1.70	3.02	4.26	5.09	0.77	2.02	3.19	4.30	5.09	0.83	1.93	3.02	4.05	4.93	5.09
C_3H_8		0.94	1.20	1.34	1.36	0.86	1.15	1.30	1.36	0.57	1.00	1.21	1.31	1.36	0.65	1.03	1.22	1.31	1.35	1.36
$i\text{-}C_4H_{10}$		0.24	0.27	0.28	0.28	0.23	0.26	0.28	0.28	0.19	0.25	0.27	0.28	0.28	0.21	0.26	0.27	0.28	0.28	0.28
$n\text{-}C_4H_{10}$		0.19	0.21	0.22	0.22	0.19	0.21	0.22	0.22	0.16	0.20	0.21	0.22	0.22	0.18	0.21	0.22	0.22	0.22	0.22
$i\text{-}C_5H_{12}$		0.11	0.11	0.12	0.12	0.11	0.11	0.12	0.12	0.10	0.11	0.12	0.12	0.12	0.11	0.11	0.12	0.12	0.12	0.12
$n\text{-}C_5H_{12}$		0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
C_6H_{14}		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_7H_{16}		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_8H_{18}		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H2O		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO_2		19.68	29.94	39.19	41.69	16.71	27.42	35.40	41.69	8.17	21.72	30.52	36.47	41.69	10.59	24.14	32.17	36.95	40.51	41.69
N2		0.18	0.45	1.80	3.05	0.11	0.26	0.71	3.05	0.03	0.09	0.18	0.44	3.05	0.02	0.05	0.10	0.18	0.88	3.05

Table 9: Effect of Temperature and Pressure Elevation Towards Separation of Components on CO2 Removal Bed 5

	Feed	Gas															
Pressure (bar)	70.00	45.00				40.00				30.00				20.00			
Temp (°C)	-30.00	-50.00	-60.00	-70.00	-80.00	-50.00	-60.00	-70.00	-80.00	-50.00	-60.00	-70.00	-80.00	-60.00	-70.00	-80.00	-90.00
CH_4	48.77	17.31	0.00	0.00	0.00	25.49	11.37	0.00	0.00	36.94	29.88	18.69	0.00	40.73	35.97	28.79	14.55
C_2H_6	5.93	0.57	0.00	0.00	0.00	0.94	0.27	0.00	0.00	1.82	0.97	0.37	0.00	2.04	1.17	0.56	0.15
C_3H_8	2.91	0.09	0.00	0.00	0.00	0.15	0.04	0.00	0.00	0.29	0.12	0.04	0.00	0.28	0.12	0.05	0.01
$i\text{-}C_4H_{10}$	0.94	0.01	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.04	0.01	0.00	0.00	0.03	0.01	0.00	0.00
$n\text{-}C_4H_{10}$	0.88	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.02	0.01	0.00	0.00
$i\text{-}C_5H_{12}$	0.73	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$n\text{-} C_5H_{12}$	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_6H_{14}	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_7H_{16}	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_8H_{18}	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H2O	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO_2	48.81	4.31	0.00	0.00	0.00	6.88	2.00	0.00	0.00	12.84	6.46	2.51	0.00	13.08	6.74	3.12	0.90
N2	0.98	0.56	0.00	0.00	0.00	0.72	0.44	0.00	0.00	0.88	0.81	0.65	0.00	0.92	0.89	0.83	0.63

	Feed	Liquid															
Pressure (bar)	70.00	45.00				40.00				30.00				20.00			
Temp (°C)	-30.00	-50.00	-60.00	-70.00	-80.00	-50.00	-60.00	-70.00	-80.00	-50.00	-60.00	-70.00	-80.00	-60.00	-70.00	-80.00	-90.00
CH_4		31.46	48.77	48.77	48.77	23.28	37.40	48.77	48.77	11.83	18.90	30.08	48.77	8.05	12.80	19.98	34.23
C_2H_6		5.36	5.93	5.93	5.93	4.99	5.66	5.93	5.93	4.11	4.95	5.55	5.93	3.89	4.75	5.36	5.78
C_3H_8		2.82	2.91	2.91	2.91	2.76	2.88	2.91	2.91	2.62	2.79	2.87	2.91	2.64	2.79	2.87	2.90
$i\text{-}C_4H_{10}$		0.93	0.94	0.94	0.94	0.92	0.94	0.94	0.94	0.91	0.93	0.94	0.94	0.91	0.93	0.94	0.94
$n\text{-}C_4H_{10}$		0.87	0.88	0.88	0.88	0.87	0.88	0.88	0.88	0.86	0.87	0.88	0.88	0.86	0.88	0.88	0.88
$i\text{-}C_5H_{12}$		0.72	0.73	0.73	0.73	0.72	0.73	0.73	0.73	0.72	0.73	0.73	0.73	0.72	0.73	0.73	0.73
$n\text{-} C_5H_{12}$		0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
C_6H_{14}		0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
C_7H_{16}		0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
C_8H_{18}		0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
H2O		0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
CO_2		44.50	48.81	48.81	48.81	41.93	46.81	48.81	48.81	35.96	42.34	46.30	48.81	35.73	42.07	45.69	47.91
N2		0.43	0.98	0.98	0.98	0.26	0.55	0.98	0.98	0.10	0.17	0.33	0.98	0.06	0.09	0.15	0.36

To characterize the best operating conditions for cryogenic packed beds, several simulation run are performed. The lowest operating pressure are maintain at high pressure to conserve the stream energy. Low temperature are used to solidify water and CO_2 for maximum separation of both component from natural gas. The schematic diagram of the finalized cryogenic packed bed network and the summary of the composition of the stream are illustrated in Figure 14 and Table 10, respectively. At the operating condition of the bed, CH_4 will remain in vapor form. The phase diagrams of the common hydrocarbons are showed in Figure 15.

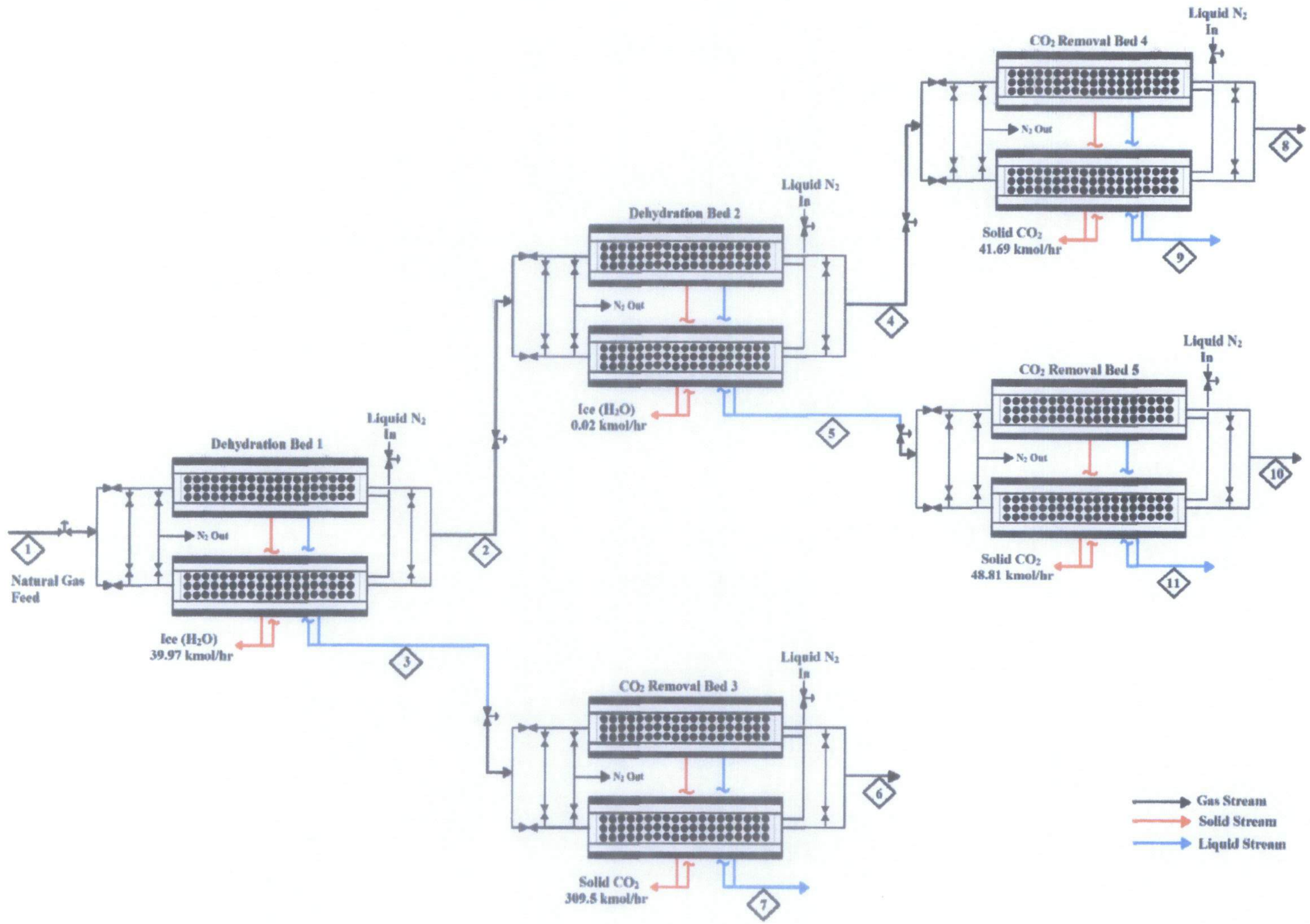

Figure 14: The Finalized Cryogenic Packed Bed Network for Water and CO_2 Separation

Table 10: Composition of Stream for High Pressure Network

Stream	1	2	3	4	5	6	7	8	9	10	11
Pressure (bar)	80	80	80	70	70	45	45	45	45	45	45
Temperature (°C)	25	-15	-15	-30	-30	-70	-70	-80	-80	-70	-70
CH_4	440.00	145.50	294.50	96.73	48.77	44.03	250.46	24.33	72.40	9.77	39.00
C_2H_6	50.00	11.01	38.99	5.09	5.93	0.40	38.59	0.25	4.83	0.15	5.78
C_3H_8	27.00	4.27	22.73	1.36	2.91	0.03	22.70	0.02	1.34	0.01	2.90
i-C_4H_{10}	10.00	1.23	8.77	0.28	0.94	0.00	8.77	0.00	0.28	0.00	0.94
n-C_4H_{10}	10.00	1.10	8.90	0.22	0.88	0.00	8.90	0.00	0.22	0.00	0.88
i-C_5H_{12}	10.00	0.84	9.16	0.12	0.73	0.00	9.16	0.00	0.12	0.00	0.73
n- C_5H_{12}	1.00	0.08	0.92	0.01	0.07	0.00	0.92	0.00	0.01	0.00	0.07
C_6H_{14}	1.00	0.05	0.95	0.00	0.05	0.00	0.95	0.00	0.00	0.00	0.05
C_7H_{16}	0.50	0.02	0.48	0.00	0.02	0.00	0.48	0.00	0.00	0.00	0.02
C_8H_{18}	0.50	0.01	0.49	0.00	0.01	0.00	0.49	0.00	0.00	0.00	0.01
H2O	40.00	0.03	39.97	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.02
CO_2	400.00	90.50	309.50	41.69	48.81	2.77	306.74	2.25	39.44	1.03	47.78
N_2	10.00	4.04	5.96	3.05	0.98	2.57	3.39	1.42	1.63	0.44	0.54

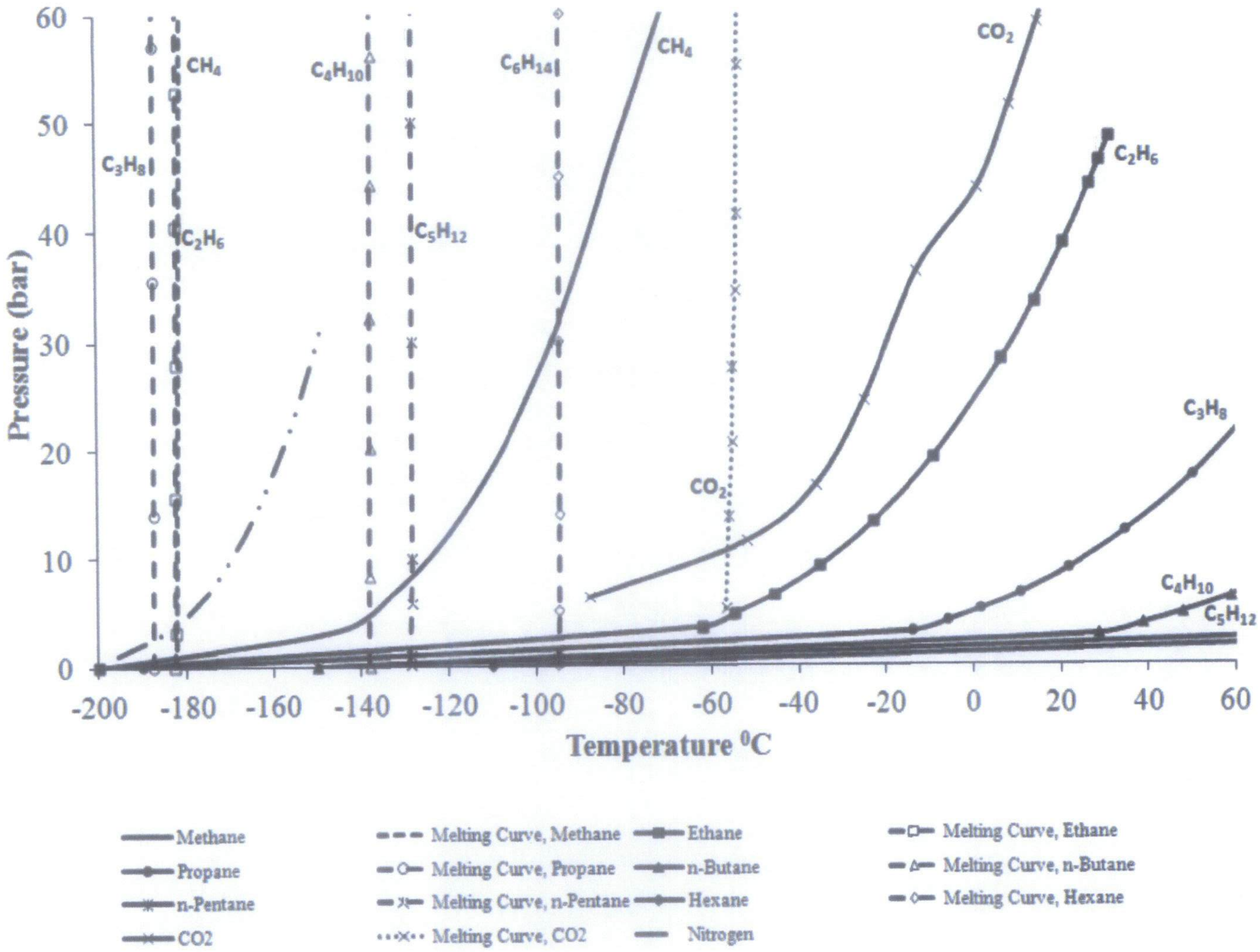

Figure 15: Phase Diagram of Common Hydrocarbons

4.2 Statistical Optimization – Atmospheric Pressure

To compare the effectiveness of the cryogenic packed bed at atmospheric pressure, statistical optimization of water and CO_2 separation from natural gas at 1 bar was performed. Each stream for this section is at 1 bar as low pressure streams are experimented for this study. The same composition of natural gas are used for this purpose but only temperature will play its role in separation process instead of temperature and pressure. The feed stream is coming at 1 bar, 25°C. Figure 16 show the schematic diagram for separation of water and CO_2 from natural gas at 1 bar.

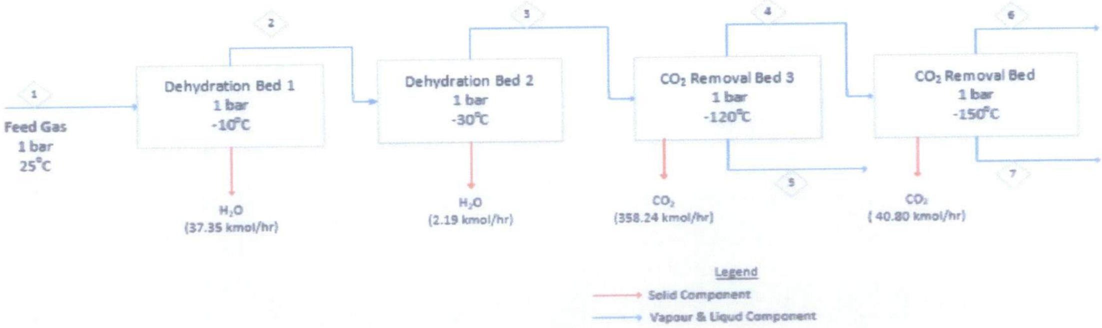

Figure 16: Cryogenic Packed Bed Networks at Atmospheric Pressure

The same configuration of separation technique for water and CO_2 removal as of high pressure network. Water in removed prior to CO_2 and multiple bed are used to maximize removal of the impurities. Since the pressure does not affect the separation, only temperature will be decreased to its purposes. The first bed is cooled down to -10°C. More than 93% of water content inside feed stream are removed from the first bed as results of water frosting on the surface of the bed. The second dehydration bed is operated at -30°C to further cooled the stream and freeze the water. Lower temperature can cause other component to changes such as higher hydrocarbon (Heptane, Octane) its phase and this can lead to hydrocarbons loss.

CO_2 removal bed is operated at -120°C because most of the CO_2 are exiting the bed as bottom product. Thermodynamic properties indicates that CO_2 starts to solidify at the temperature of -90°C.But in order to maximize the separation of CO_2

and to reduce hydrocarbon loss, -120°C is chosen. For the last bed, lower temperature of -150°C are applied. More CO_2 solidify on the surface of the packing. Due to the mixture properties of the stream, more CO_2 will be removed from the stream at this lower temperature as compared to normal pure component's freezing point. As results, lean natural gas is obtained from the bottom and top product of the bed. The summary of the stream's composition and the finalized schematic diagram of cryogenic packed bed network at atmospheric pressure are illustrated in Table 11 and Figure 17, respectively.

Table 11: Composition of Stream for Cryogenic Packed Bed Network at Atmospheric Pressure

Stream	1	2	3	4	5	6	7
Pressure (bar)	1	1	1	1	1	1	1
Temperature (°C)	25	-10	-30	-120	-120	-150	-150
CH_4	440.000	440.00	440.00	431.04	8.96	420.01	11.03
C_2H_6	50.000	50.00	50.00	18.51	31.49	1.62	16.88
C_3H_8	27.000	27.00	26.99	0.60	26.39	0.00	0.60
i-C_4H_{10}	10.000	10.00	9.99	0.02	9.96	0.00	0.02
n-C_4H_{10}	10.000	10.00	9.98	0.01	9.97	0.00	0.01
i-C_5H_{12}	10.000	10.00	9.93	0.00	9.93	0.00	0.00
n- C_5H_{12}	1.000	1.00	0.99	0.00	0.99	0.00	0.00
C_6H_{14}	1.000	1.00	0.94	0.00	0.94	0.00	0.00
C_7H_{16}	0.500	0.50	0.39	0.00	0.39	0.00	0.00
C_8H_{18}	0.500	0.50	0.20	0.00	0.20	0.00	0.00
H2O	40.000	2.65	0.46	0.00	0.46	0.00	0.00
CO_2	400.000	399.98	399.97	41.73	358.24	0.93	40.80
N_2	10.000	10.00	10.00	9.98	0.02	9.97	0.01

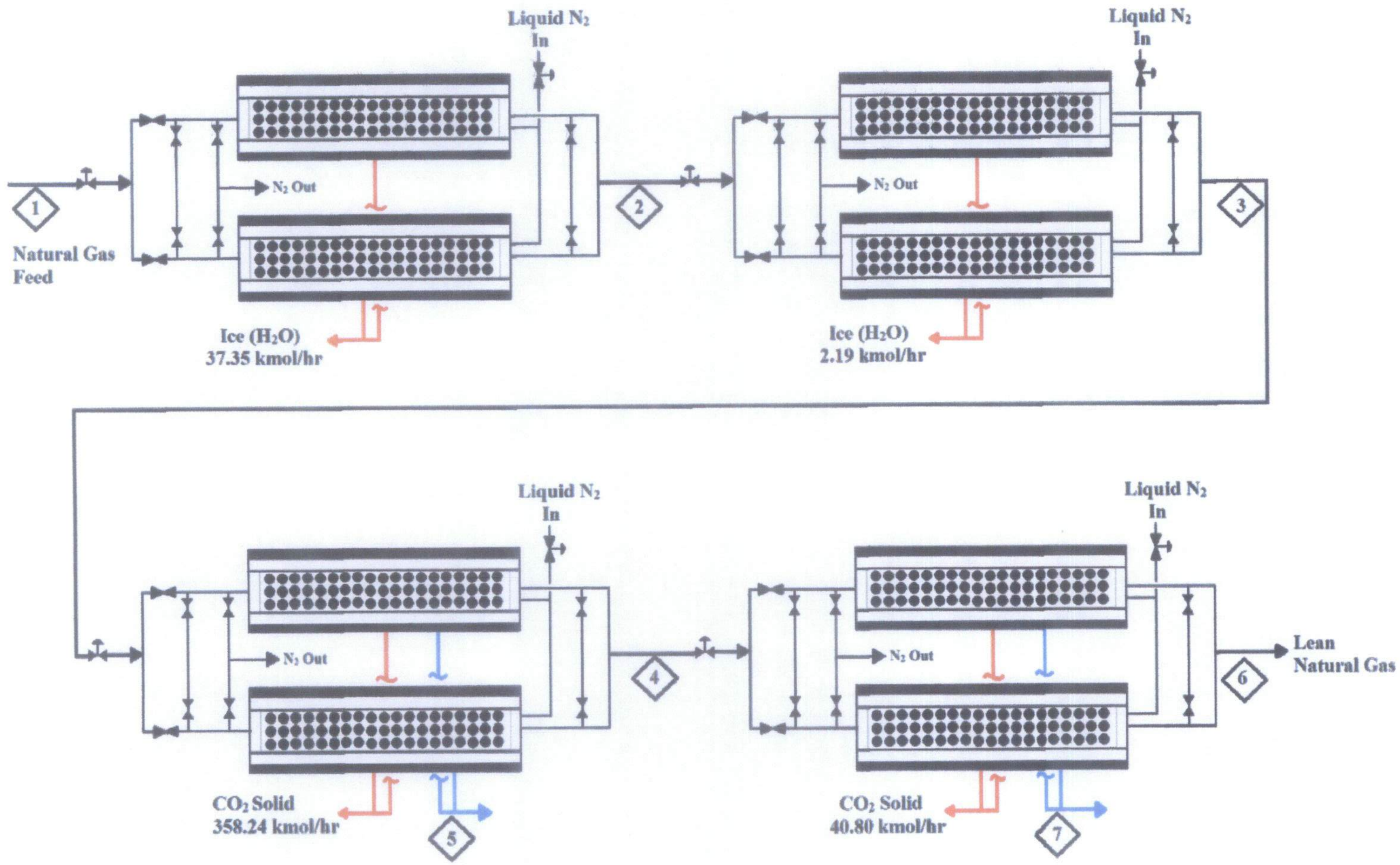

Figure 17: Finalized Schematic Diagram of Cryogenic Packed Bed Network At Atmospheric Pressure

The results obtained from the statistical optimization are used to be further verified in experimental study. The temperature range of 0°C to -30°C are used for dehydration process and the lower temperature of -110°C are applied for CO_2 removal. The experimental results for this study will be displayed in the next section.

The detailed of the temperature effect on the stream of atmospheric pressure can be found in Appendix section.

4.2 Experimental Study

Dehydration

1. Effect of Initial Bed Temperature

The initial bed temperature gave significant effect on dehydration using Case 1. Five initial bed temperature are studied, ranging from 0°C to -30°C. Constant water inlet to the bed are kept at 14.7 g/m^3 of gas. In the first run (0°C) the cumulative water content obtained after 35 seconds is 0.0053 kg. Meanwhile for the lowest temperature of -30°C, the cumulative water content increase significantly to 0.00068 kg. This proves that initial bed temperature does give meaningful effect in removal of water from gas feed stream. Lower initial bed temperature capture more water.

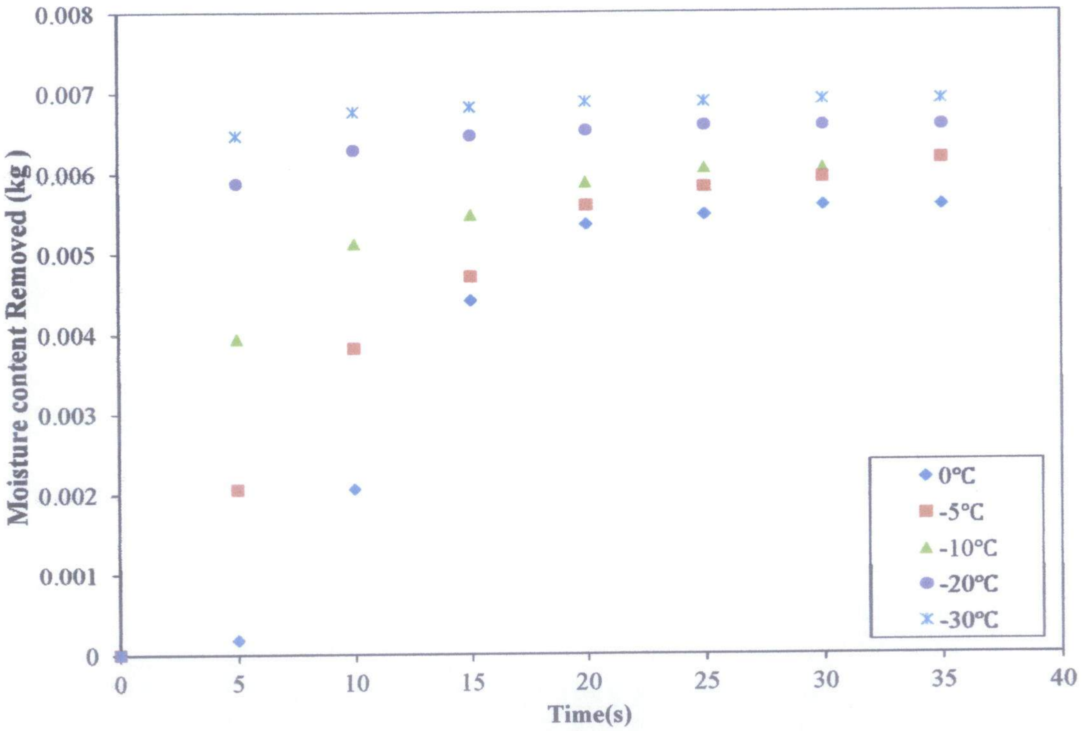

Figure 18: Effect of Bed Temperature

CO_2 Capture Using Cryogenic Packed Bed

The effect of bed temperature and inlet concentration for CO_2 separation using pure CO_2 stream has been conducted. CO_2 concentration at outlet of the bed is analyzed and time was recorded to investigate the different parameter.

1. Effect of Bed Temperature

The temperature of the bed plays an important role in CO_2 removal in cryogenic packed bed. As the flow rate and composition of feed gas are constant, higher temperature indicates that the change in bed temperature with CO_2 freezing point (-78°C) is higher. Thus the time taken for bed saturation will be higher as the temperature of the bed decrease. More CO_2 captured due to higher difference in bed temperature and CO_2 freezing point. Figure 19 illustrates the effect of bed temperature towards separation of CO_2 from the gas stream.

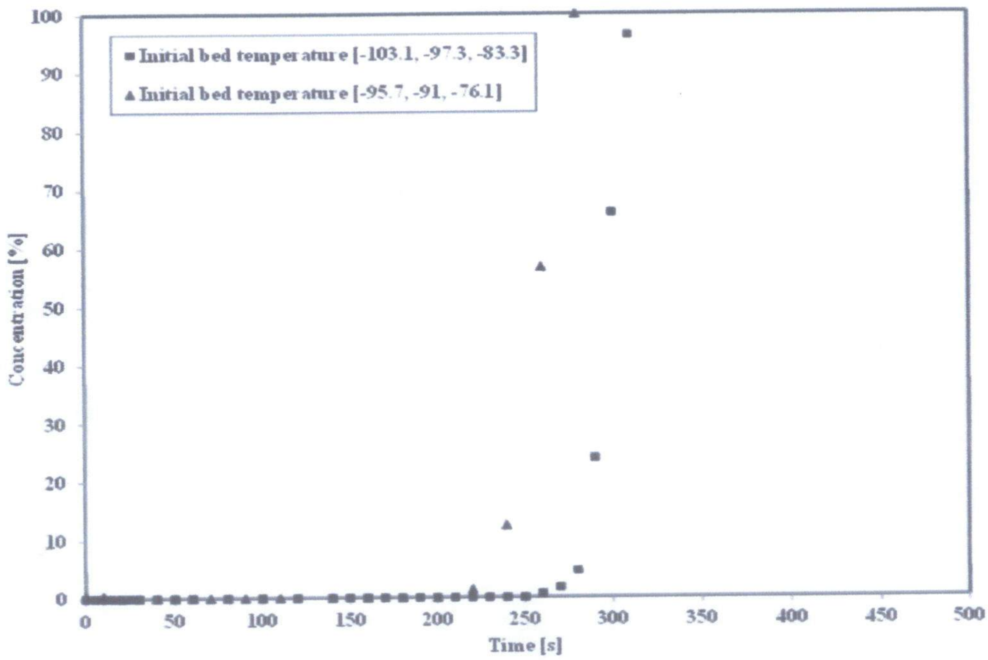

Figure 19: Effect of Bed Temperature on CO_2 separation

2. Effect of Feed Flow Rate

The effect of feed flow rate of feed gas to the cryogenic packed bed are studied at constant bed temperature and composition of feed gas. Flow rate of 15 litre per minute and 5.3 litre per minute are used. As results, higher feed flow rate takes less time for the bed to saturate. This is because higher flow rate indicates more CO_2 flow into the bed. this means that more energy is transferred from CO_2 to the bed. This results in less bed saturation time. The effect of feed flow rate in illustrated in Figure 20:

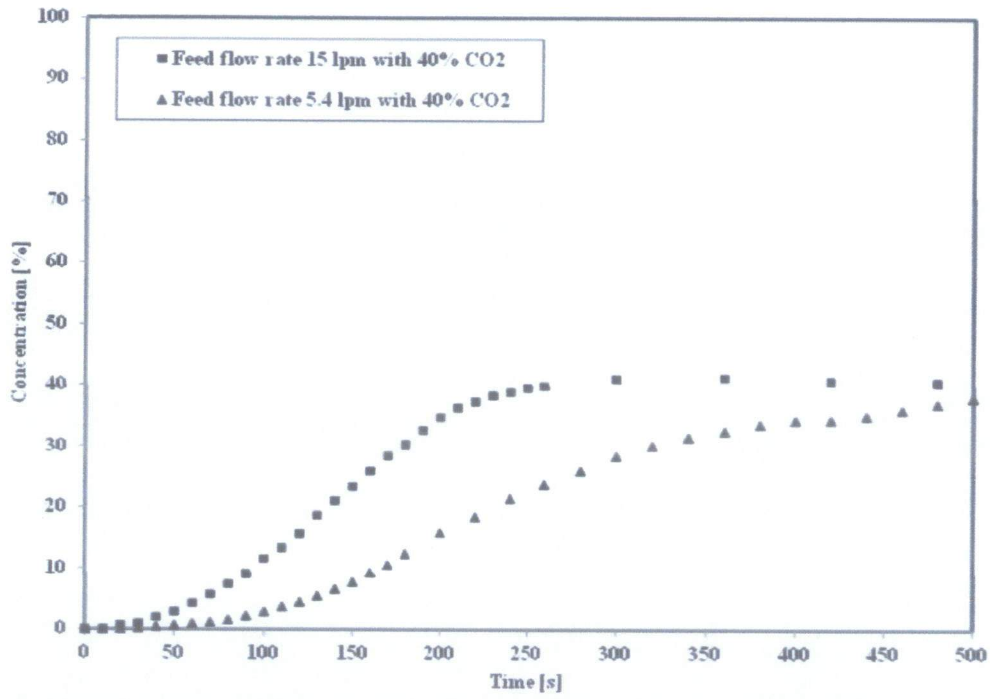

Figure 20: Effect Of Flow Rate on CO_2 separation

3. Effect of Inlet CO_2 Concentration

The effect of inlet gas pass through the cryogenic packed bed was experimented at constant flow rate. 6 different concentration of CO_2 are studied, which all of them contain high CO_2 concentration in feed gas, from 20% to pure CO_2 stream. This is to simulate the high concentration of CO_2 in natural gas field in Malaysia. The result shows that high CO_2 content in the gas feed took more saturation time as compared to lower concentration feed. This phenomenon is due to more CH_4 contain in low CO_2 concentration feed and resulting in more heat take up from the bed to the gas. Freezing point of CH_4 is much lower than that of CO_2. So longer saturation time is need for higher CO_2 concentration in the feed gas. The effect of inlet CO_2 concentration is illustrated in Figure 21.

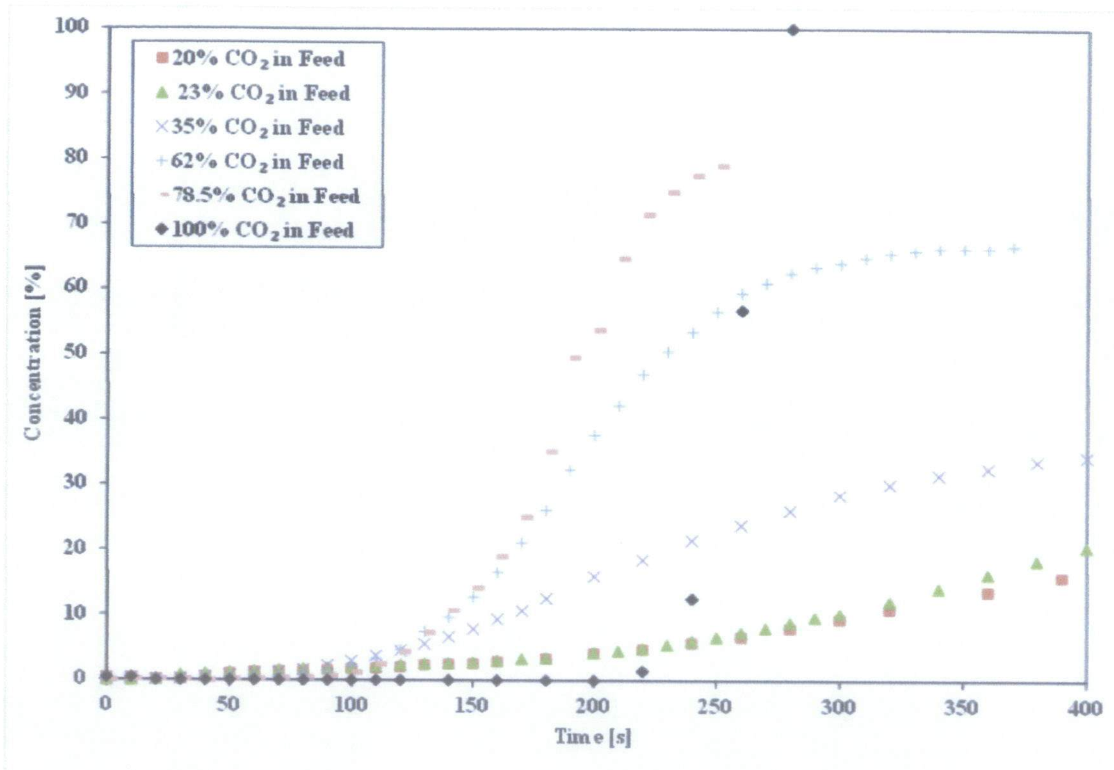

Figure 21: Effect of CO_2 Concentration in Feed Gas on CO_2 Separation

CHAPTER 5

CONCLUSION & RECOMMENDATION

This work has proposed a state-of-the-art CO_2 and H_2O removal methodology from natural gas using multiple cryogenic packed beds. The concept of operation and advantages of low temperature CO_2 and H_2O separation have been discussed in detail. One of the advantages for this process is dehydration and natural gas sweetening in a series of single process using multiple cryogenic bed. The effect of temperature, flow rate and concentration in dehydration and CO_2 removal was thoroughly studied. Statistical optimization of these parameter also been compared with experimental data. In conclusion, bed temperature, gas feed flow rate and concentration of gas feed gave significant results in dehydration and CO_2 removal. The high CO_2 content in natural gas is suitable to be processed with cryogenic packed bed.

For future work, cryogenic separation of water and CO_2 should be studied at higher pressure stream. This is to imitate the real industrial scenario where high pressure flow line are fed into the processing facility.

REFERENCES

Ali, A. H., Ganguly, S., & Shariff, A. B. (2013), Simulation of Cryogenic Packed Bed Using 1-Dimensional Pseudo Homogenous Model, *International Oil & Gas Symposium and Exhibition (IOGSE 2013),* Sabah, Malaysia.

Ali, A. H., Hii, K., Redza, A., Shariff, A. B., & Ganguly, S. (2013), Multiple Bed Dehydration and Carbon Dioxide Removal from Natural Gas Using Cryogenic Separation Process.

B.T. Kelly, J. V. (2011), Controlled Freeze Zone for developing sour gas reserves, *Energy Procedia.*

Berstad, D. N. (2012), Low-temperature CO2 removal from natural gas, *Energy Procedia 26.*

David Berstad, P. N. (2012), Low- Temperature CO2 removal from Natural Gas, *Energy Procedia.*

Engineer, S. o. (2004), Optimisation CO2 Removal Design For Block B-17 in MTJDA, *SPE Asia Pacific Oil and Gas Conference and Exhibition.*

Ewan, D. L. (1975), Investigating the Feasibility of a Cryogenic Turbo-Expander Plant, *54th GPA Annua Convention,* Houston.

Gandhidasan, G. A.-F.-M. (2000), Dehydration of natural gas using solid desiccants, *Energy 26.*

Harold G. Donnelly, D. L. (1954), Phase Equilibria in the Carbon Dioxide- Methane System, *Industrial And Engineering Chemistry.*

Lavik, V. F. (2009), Freeze out in natural gas systems.

Leuven. (2007), International Institute of Refrigeration, *International Institute of Refrigeration,* Peeters Publishers.

Heat and Mass Transfer

1) Effective axial heat dispersion in transient packed bed reactor.

$$\boxed{\lambda_{eff} = \lambda_{bed,0} + \frac{Re\,Pr\,\lambda_g}{Pe_{ax}} + \frac{Re^2\,Pr^2\,\lambda_g}{6(1-\varepsilon_g)Nu}} \quad [5]$$

Where Pe_{ax} is calculated as follows

$$\boxed{Pe_{ax} = \frac{2p}{1-p}, \quad p = 0.17 + 0.33\exp^{-24/Re}} \quad [6]$$

2) Heat transfer coefficient between gas to particle is given by:

$$\boxed{Nu = (7 - 10\varepsilon_g + 5\varepsilon_g^2)(1 + 0.7\,Re^{0.2}\,Pr^{1/3}) + (1.33 - 2.4\varepsilon_g + 1.2\varepsilon_g^2)\,Re^{0.7}\,Pr^{1/3}} \quad [7]$$

3) For mass, they are dispersed inside the reaction according to the following equation

$$\boxed{\frac{D_{eff}}{v_g d_p} = \frac{0.73}{Re\,Sc} + \frac{0.5}{\varepsilon_g\left(1 + \frac{9.7\varepsilon_g}{Re\,Sc}\right)}} \quad [8]$$

Mass of Rate Deposited

1) In our system, the rate of CO_2 desublimate at the packing material can be calculated as follows

$$\boxed{\dot{m}_i'' = \begin{cases} g(y_{i,s}p - p_i^\sigma) & \text{if } y_{i,s}p \geqslant p_i^\sigma \\ g(y_{i,s}p - p_i^\sigma)\dfrac{m_i}{m_i + 0.1} & \text{if } y_{i,s}p < p_i^\sigma \end{cases}} \quad [9]$$

Nasir, D. R. (2006), "Technical Challenges and Solutions on Natural Gas Development in Malaysia, Beijing, China.

Netusil, M. D. (2011), Comparison of three methods for natural gas dehydration, *Journal of Natural Gas Chemistry*.

Ozturk, M. (2010), Modelling Vapor-Liquid-Solid Phase Behavior in Natural Gas Systems.

Roussak, O. V. (2013), *Applied Chemistry: A Textbook for Engineers and Technologists*, Springer.

Shimekit, B., & Mukhtar, H. (2012), Natural Gas Purification Technologies - Major Advances for CO2 Separation and Future Directions, *Advances in Natural Gas Technologies*.

The Future of The Gas Industry in Malaysia. (2013), Retrieved December 2013, from Gas Malaysia: http://www.gasmalaysia.com/about_gas/future_gas_industry.htm

Tuinier, M. A. (2009), Cryogenic CO2 Capture Using Dynamically Operated Packed Bed, *Chemical Engineering Science*.

Wen, C. C. (2011), Evaluation of natural gas dehydration in supersonic swirling separators applying the Discrete Particle Method, *Advanced Powder Technology*.

ZareNezhad, B. E. (2006), Application of Peng- Robinson equation of state for CO2 Freezing Prediction of Hydrocarbons mixtures at cryogenic Conditions of Gas Plant, *Cryogenic*.

APPENDIX

One dimensional Pseudo-Homogenous

1- In gas phase, the mass balance is given by:

$$\boxed{\varepsilon_g \rho_g \frac{\partial \omega_{i,g}}{\partial t} = -\rho_g v_g \frac{\partial \omega_{i,g}}{\partial z} + \frac{\partial}{\partial z}\left(\rho_g D_{eff} \frac{\partial \omega_{i,g}}{\partial z}\right) - \dot{m}_i'' a_s + \omega_{i,g} \sum_{i=1}^{n_C} \dot{m}_i'' a_s} \qquad [1]$$

2- For solid phase, the mass balance is:

$$\boxed{\frac{\partial m_i}{\partial t} = \dot{m}_i'' a_s} \qquad [2]$$

3- Total continuity equation for gas phase:

$$\boxed{\frac{\partial(\varepsilon_g \rho_g)}{\partial t} = -\frac{\partial(\rho_g v_g)}{\partial z} - \sum_{i=1}^{n_C} \dot{m}_i'' a_s} \qquad [3]$$

4- For overall process, the energy balance consisting of both phase is given by

$$\boxed{(\varepsilon_g \rho_g C_{p,g} + \rho_s (1-\varepsilon_g) C_{p,s}) \frac{\partial T}{\partial t} = -\rho_g v_g C_{p,g} \frac{\partial T}{\partial z} + \frac{\partial T}{\partial z}\left(\lambda_{eff} \frac{\partial T}{\partial z}\right) - \sum_{i=1}^{n_C} \dot{m}_i'' a_s \Delta h_i} \qquad [4]$$

2) As our system consist of two phase of solid and gas, the equilibrium as the solid CO_2 deposited can be figure out using equation as per follows:

$$\boxed{\begin{aligned} &p^{e}_{CO_2}(T) = \exp\left(10.257 - \frac{3082.7}{T} + 4.08 \ln T - 2.2658 \times 10^{-2} T\right) \\ &\Delta h^{sub}_{CO_2} = 5.682 \times 10^{5}\ \mathrm{J/kg} \end{aligned}} \quad [10]$$

Boundary Conditions

The assumption has been made which is our system is steady state for transient flow. It take account the stagnation specific enthalpy, H and stagnation pressure, p_o.

$$p_0 A = pA\left(1 + \frac{1}{2}(\gamma - 1)\frac{u^2}{a^2}\right)^{\gamma(\gamma-1)^{-1}} \quad [11]$$

Nomenclature

t	Time, s
v	Superficial velocity, m/s
z	Axial co-ordinate, m
D_{eff}	Effective diffusion coefficient, m^2/s
$\dot{m}''$	Mass deposition rate per unit surface area, $kg/m^2/s$
a_s	Specific solid surface area per unit bed volume, m^2/m^3
C_p	Heat capacity, J/kg/K
T	Temperature, K, °C
m	Mass deposition per unit bed volume, kg/m^3

- Greek letters

ε	Bed void fraction
ρ	Density, kg/m^3
ω	Mass fraction, kg/kg
λ_{eff}	Effective conductivity, W/m/K
Δh_i	Enthalpy change related to the phase change of component i, J/kg

- Subscripts

0	Initial
g	Gas phase
s	Solid phase
i	Component i